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VOL. 14, SEC. A. AUGUST, 1936 NUMBER 8

ALKALI METAL FILMS TRANSPARENT IN THE SCHUMANN REGION[1]

BY W. H. WATSON[2] AND D. G. HURST[3]

Abstract

Sodium and potassium films deposited from a molecular beam on fluorite at liquid air temperature have been found to be transparent in the Schumann region. For $\lambda > 1400$ Å no transparency has been found in the case of lithium. A technique for producing these films is described. The theoretical bearing of these results is discussed.

It is well known from the experiments of R. W. Wood (12, 13), that the alkali metals when deposited as coherent films on quartz are transparent to ultra-violet light of wave-length less than the fairly well defined value characteristic of each metal, *viz.*, caesium 4400, rubidium 3600, potassium 3150, sodium 2100, lithium 2050 Å. Wood reported that all the metals, with the possible exception of caesium, are transparent to ultra-violet light of wave-length 1860 Å or greater. The experimental facts have been considered from the point of view of the theory of electrons in solids (3, 14), and in this connection it seemed to the writers desirable to extend experimental knowledge by investigating the transmission of light in the Schumann region through films of some of these metals. The present paper describes the technique developed by the writers for producing coherent films on fluorite before the slit of a vacuum spectrograph, and gives an account of the results obtained with sodium, potassium and lithium. A notice of the results with sodium and potassium has already appeared in Nature (10). So far the writers have not attempted to measure absorption coefficients.

Apparatus

The apparatus consists of three main sections: (i) the vacuum grating spectrograph (Hilger E50); (ii) the light source (the hydrogen discharge tube already described in this Journal (9)); and (iii), between (i) and (ii), separated from them by fluorite windows, the chamber in which the films are prepared. We shall call this third section the alkali-metal chamber. It is shown in Fig. 1. The upper left is a section perpendicular to the light beam; the upper right is the vertical section containing the light beam; and the lower left is the horizontal section containing the light beam. Metal is shaded

[1] *Manuscript received June 30, 1936.*
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diagonally, glass is left clear, fluorite is cross-hatched. The end of the discharge tube is shown in the upper right section above *H*.

The alkali metal is deposited on fluorite cooled to liquid air temperature. *A* is a tube to hold the liquid air, and the fluorite is held in the metal support

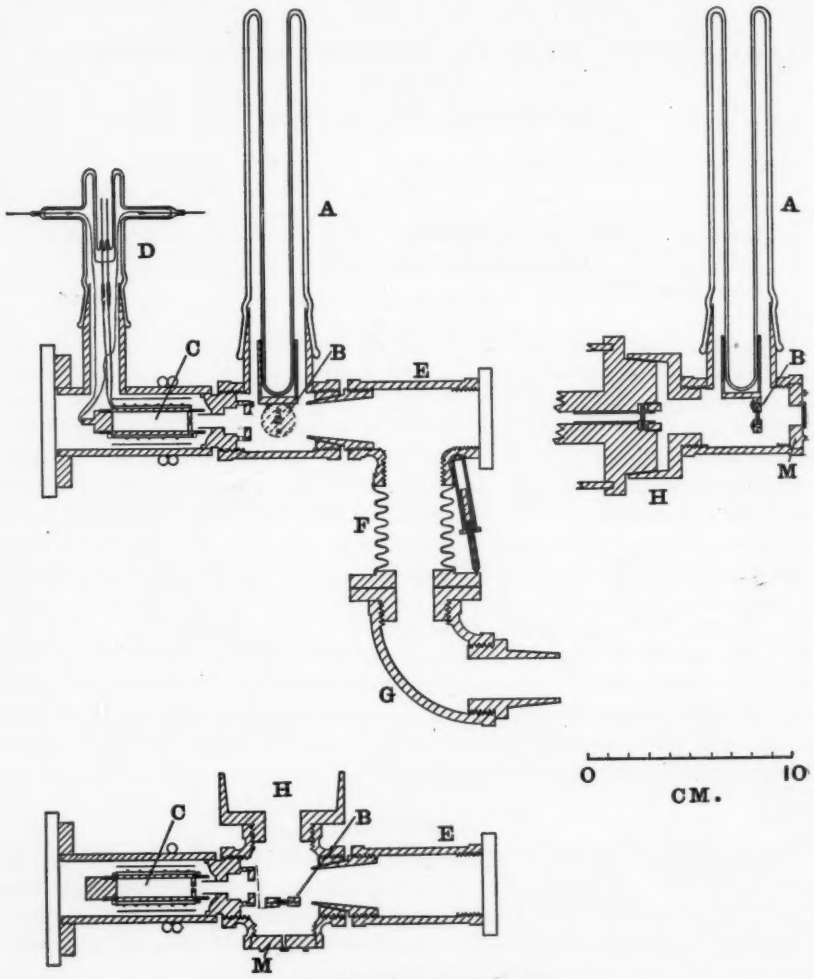

FIG. 1. *The alkali-metal chamber.*

B which slips over a copper sleeve on *A*. The copper was formed electrolytically on the silvered glass and turned in the lathe. The metal film is deposited when *A* is rotated so that the fluorite faces the oven *C* which is a steel tube supported on a light framework of Pyrex. The oven is heated by a coil of tungsten wire wound on a Pyrex tube fitting over the oven, and its temper-

ature is known by means of a thermocouple. This arrangement is quite suitable for all the alkali metals except lithium. For this metal, the oven is supported on tungsten wires and is heated by electron bombardment. The enveloping chamber, constructed wherever possible from plumbing fittings, is evacuated by its own pumping system consisting of an oil diffusion pump backed by a Hyvac. Wax seals are used to make connections except on the cone at *A* which is sealed with grease.

In order to give the freedom necessary in aligning the light source with the spectrograph, a "sylphon" *F* forms part of the pump line and the final connection is made by waxing together the brass plates on *F* and *G*, the latter being rigidly fixed. The slit of the spectrograph is enclosed when *M* presses against the end of the spectrograph and is sealed with plasticine.

The discharge tube described previously (9) has been altered in the following respects—a Pyrex tube is fitted into the exit hole to decrease sputtering, and the fluorite window is protected by a disc of glass with a hole in its centre. These are shown in Fig. 1. The writers found that great care is necessary in making and mounting the capillary of the discharge tube, otherwise fracture occurs after a short period of running.

Procedure

Sodium and potassium were triply distilled *in vacuo* and sealed into small tubes each of which contained about 0.05 gm. The alkali-metal chamber was filled with nitrogen, opened behind the oven and a stream of gas allowed to pass through. The glass tube containing the charge for the oven was broken open at both ends, placed in a helix of nichrome wire in which the metal was electrically heated, and as soon as it melted was forced by an iron plunger into the oven. The system was closed and evacuated. The oven was warmed to a suitable temperature (about 300° C. for sodium, 200° C. for potassium) found approximately by calculation to give deposition of metal at the rate of 100 atomic layers a minute. The fluorite surface at *B*, on which the film was to be deposited, was exposed to light from the hydrogen tube in order to clean it (7). The fluorite was then turned to face the oven and exposed for 10 min. at least. In order to ensure that enough metal had been deposited, the film was turned into the path of the light, and unless thicker films were desired the film was considered complete when the visible central image had been extinguished. The thinnest films were of the order of 1000 atomic layers. Unless the fluorite was cooled to liquid air temperature the writers did not succeed in making proper films. At higher temperatures the films were not coherent.

The photographs were taken on process film oiled with Nujol (4, p. 61).

Results

Examples of the spectra for sodium and potassium films have already been published (10). The whole spectrum transmitted by sodium could be photographed on one film with the proper setting of the grating. It was found that transmission began at 2100 Å and continued throughout the Schumann

region,—photographs with films of different thicknesses indicated that there is some absorption in the range 1400–1250 Å. In order to establish that the potassium films were proper ones, the practice was adopted that after the photograph of the Schumann region had been made, the grating was turned so as to show 3100 Å about the middle of the spectrum. Weak absorption by potassium films begins about 1700 Å and increases to the short waves. In the case of lithium the authors have made what they believe are good films and have not succeeded in obtaining evidence of their transparency, although weak transmission of wave-lengths less than 1400 Å might have escaped detection because of the weakness of their spectrum in this region (due to the large number of surfaces traversed by the light, cf. (6)). For the metals sodium, potassium, rubidium, caesium, the critical wave-length is proportional to the square of the lattice constant (8), and this leads one to expect no transparency in lithium for wave-lengths > 1400 Å. The transmission beginning at 2050 Å reported by Wood does not fit this law.†

The short wave ends of the transmission bands have wave-lengths roughly proportional to the *first* power of the lattice constant (a). This is shown in Table I. The choice of λ is decidedly arbitrary; nevertheless it is difficult to make the choice so as to fit the square law, because 1860 Å for caesium is probably an overestimate. It may be pointed out that the same relation holds between the lattice constant and the long wave end of the absorption spectrum (1, p. 434) for the series of alkali halides sodium fluoride, potassium chloride, rubidium bromide*, which correspond to the metals sodium, potassium and rubidium with respect to closed electron shells. Indeed the actual wave-lengths at which absorption begins for the halides are not very different from those for the corresponding metals. It is also striking that for both series the onset of absorption is a gradual one. These facts suggest that the closed shell structures determine the optical properties for these wave-lengths. If this is the case the most recent form, advanced by Wilson (11), of the theory of the optical properties of metals will not apply to the alkali metals, which ought to offer the best chance for the successful application of a theory based on the free electron model. The first two absorption bands of the metal crystallizing in the body-centered cubic system, according to the theory, are given in Table II where the frequency ν is expressed in terms of $h/2ma^2$, where h = Planck's constant, m = mass of electron, a = lattice constant (side of

TABLE I

—	a (Å)	λ (Å)	λ/a
Cs	6.13	1860	303
K	5.32	1500	282
Na	4.28	1250	292

† *Note added in proof. In a letter to one of the writers Professor Wood has kindly stated that he has believed for some time that his supposed lithium films were really sodium.*

* *Lithium would have to be compared with lithium hydride and caesium with caesium iodide. The data for the former are not available and the latter is body-centered (type B_2), whereas the other halides are face-centered cubic (type B_1).*

elementary cube). The experimentally observed transmission extends from 0.73 to about 1.25 on the same scale, the latter figure varying with a. The first theoretical absorption band overlaps the transmission band actually observed, and the second absorption band is too far in the ultra-violet to explain the absorption observed to begin in the Schumann region. On the other hand, Kronig's theory (3) of the transmission (a modification of Zener's application (14) of classical optical theory) is supported by recent measurements of the optical properties of potassium in the near ultra-violet by Ives and Briggs (2)*. Kronig's theory provides the small absorption by the metal necessary for the photoelectric effect without introducing the lattice structure of the crystal, whereas Wilson's theory depends essentially on this structure. The critical wave-length for the beginning of transmission in the near ultra-violet is, according to Kronig and Zener, proportional to $a^{3/2}$, but agreement with experiment (a^2) can be achieved by a plausible adjustment (2). If this be accepted, the mechanism of Kronig appears to give a good account of the role of free electrons in determining the optical properties of the alkali metals in the near ultra-violet. It appears to the writers that in the far ultra-violet it is necessary to consider the metal on the same basis as insulating crystals, and to depend on "bound electrons" to explain the observed optical absorption.

TABLE II

Band number	ν min.	ν max.
1	0.24	3.76
2	1.52	6.50

Acknowledgment

The writers wish to thank Dr. A. N. Shaw for his kind interest in this work.

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* *The agreement with experiment claimed by Sergeiev and Tchernikovsky (5) cannot be accepted as significant.*

INTENSITY MEASUREMENTS IN THE DIFFRACTION OF LIGHT BY ULTRASONIC WAVES[1]

By F. H. Sanders[2]

Abstract

Measurements of the distribution of light energy among the various orders of the diffraction pattern produced when monochromatic light is passed through a liquid subjected to high-frequency ultrasonic disturbances have been carried out over a range of ultrasonic intensities at frequencies in the region of 5 megacycles per second. Both progressive and standing wave fields have been studied. Results of the experiments show excellent agreement with the theory of Raman and Nath for the variation in degree of scattering with varying ultrasonic intensity. Absolute measurements of the sound intensity conducted with a torsion pendulum are in good agreement with that expected from the theory for the liquids and light wave-lengths involved.

Introduction

The possibility of producing diffraction of light in a transparent medium subjected to periodic variations in density was predicted by L. Brillouin (9) in 1921. It was not until 1932 that an experimental demonstration of the phenomenon was realized by Debye and Sears (11) in the United States and by Lucas and Biquard (13) in France. The method pursued by both sets of investigators was the production of ultrasonic waves of very high frequency (10^6 to 10^7 cycles per second) in liquids by the use of the vibrations of a piezoelectric crystal. When a beam of parallel light was passed through the liquid in a direction normal to the direction of propagation of the ultrasonic disturbance, the light was scattered as by a plane diffraction grating. One of the interesting features observed was that, while Brillouin's theory had predicted the appearance of a single order of diffraction, the experiments showed a number of orders scattered according to the simple grating formula,

$$n\lambda = d \sin \theta$$

where d, the grating space, is equal to the wave-length of the ultrasonic disturbance in the liquid.

In an attempt to explain the divergence between theory and experiment a number of theoretical analyses dealing with the diffraction of light in a progressive wave field have been published. Debye (12) again obtained a result indicating the presence of a single order of diffraction. As an explanation of the multiple orders actually observed, Debye suggested that possibly a non-linear relation between density and dielectric constant might exist at high frequencies, or that the presence of harmonics in the vibration of the piezoelectric crystal might produce a number of single-order diffraction patterns of appropriate dispersion. Lucas and Biquard (14, 15) have pointed out that both proposals are unlikely, the first because of the relatively small pressure amplitudes involved, and the second because of the fact that a piezoelectric crystal will resonate only on odd harmonics.

[1] *Manuscript received July 7, 1936.*
Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

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The latter writers have developed a theory (14, 15) based on a mirage effect, in which they obtain the amplitude and phase of an individual light ray as it progresses through the disturbed medium. This theory predicts multiple orders, the number of which increases with the length of path in the medium and the ultrasonic intensity. The distribution of light energy predicted by the above-mentioned theory, however, for path lengths and ultrasonic intensities where the light rays have not reached a focus in the sound field, is such that the relative intensities of the orders decrease monotonically with increasing order number. That this is not always the case has been shown experimentally by R. Bär (2). Under certain conditions of intensity, path length and optical wave-length, Bär has observed patterns in which some orders have far lower intensities than those of higher number.

Brillouin (10), enlarging on his earlier analysis, has also developed a theory giving multiple orders, but the mathematical difficulties restrict the application of the theory to the case where the intensity of the first order is still small compared with that of the central order.

In some very recent papers Raman and Nath (16, 17) have treated the scattering of light by a periodically disturbed medium in a manner analogous to that developed by Rayleigh for the diffraction of a plane wave incident normally on a periodically corrugated surface. The results of these theories are very interesting in that, in addition to predicting a dependence of the spectral character of the diffracted light on the number of the order both for progressive and standing waves, a type of distribution of the relative intensities of the various orders of light scattered by a standing wave field is obtained which differs very markedly from that to be expected with progressive waves. The scattering patterns for the progressive wave case appear to be in good qualitative agreement with those photographed by Bär.

H. Becker (5) has recently published a paper in which Debye's theory, with some modification, is compared with the results of an experimental study of the variation in intensity of the first order with ultrasonic intensity. For low sound intensities the agreement is quite good.

The present paper is a description of an investigation of the relative intensities of the various orders for ultrasonic intensities ranging from zero to values sufficiently high to give five or six orders of measurable intensity in both standing and progressive wave fields.

Experimental

Two different quartz crystals, one having a fundamental frequency of 370 kc. and the other of 448 kc., were used alternatively as a source of ultrasonic vibrations. The faces of the crystals were silvered chemically and copper-plated to ensure a continuous conducting surface. The crystal in use was supported vertically in the liquid by means of light phosphor-bronze contacts and excited by a "push-pull" oscillator employing two 200-watt Mullard transmitting tubes.

A Zeiss electric sodium vapor lamp operated on batteries provided a very steady and intense source of monochromatic light. A parallel beam of light

of dimensions 10 mm. by 10 mm. was passed through the sound field and focused upon a screen containing a narrow slit of such dimensions as to receive the light from a single order. Intensity measurements were effected by means of a photoelectric cell mounted behind the slit, the slit and photo-cell being movable transversely across the diffraction pattern. Since the light intensities frequently fell to very low values, a d-c. amplifier was used in conjunction with the photo-cell. The characteristic curve of the combination of cell and amplifier was obtained by the use of an inverse-square bench, and it proved to be quite linear over the range of light intensities concerned.

Several methods were used in the measurement of ultrasonic intensity. A high resistance in series with a vacuum thermocouple was connected across the crystal holder, and the square of the applied voltage read directly by means of a microammeter. Following some preliminary experiments that indicated the need of an intensity-measuring device that could be more readily adjusted to suit various intensity ranges, it was found more convenient to use a tuned circuit loosely coupled with the oscillator. When checked against each other these two methods showed excellent linear agreement.

As an additional check on the ultrasonic intensity measurements, a torsion pendulum was constucted which could be placed in the sound field just beyond the intersection of the light beam with the field. The pendulum vane was maintained in a vertical plane by a light but rigid shaft with bearings above and below, and was connected by a fine tungsten suspension to a calibrated torsion head. Since the torsion pendulum, having a measured reflection coefficient very close to 100% at the frequencies used, would set up standing waves when placed in the field, measurements with the pendulum were made only in the case of standing wave fields. The torsion pendulum was in all cases located very near the reflector producing the standing wave field; consequently the sound intensity in the field when the torsion pendulum vane was parallel to the crystal should not be appreciably different from that due to the reflector alone. This point was checked by measurement of the intensity of the central diffraction order with the reflector alone in place and with the pendulum vane in the parallel position. The photo-cell currents for the two cases checked to well within the errors of measurement. The force producing the deflections of the torsion pendulum should be due to the radiation pressure and hence directly proportional to the ultrasonic intensity. In the measurements, the torsion head was set at a definite angle and the output of the crystal adjusted until a balance was obtained. This eliminated any change in output due to the added capacity introduced by the presence of the operator's hand on the torsion head. Curves of torsion head settings were plotted against microammeter readings obtained by the two earlier methods and in all cases gave excellent straight lines. In addition to serving as a check on the linearity of the electrical measurements of relative ultrasonic intensity, the torsion pendulum provided a means of effecting an approximate determination of the absolute intensities involved.

Because of the difficulty of completely eliminating standing waves in a container of ordinary dimensions, the first portion of this investigation was

carried out with a standing wave field. The container used was a small biological cell of white mirror glass, 10 cm. in length. One end of the cell served as the reflecting surface and, by the use of a universal mount, could be set parallel to the face of the crystal. The crystal, also in a universal mount, could be adjusted quite independently of the reflector. In addition the whole system could be rotated as a unit about a vertical axis through the centre of the intersection of light beam and sound field. By means of a slow motion screw the reflector could be moved in the direction of propagation of the ultrasonic waves so that the optimum standing wave condition could be realized. Actually it was found that with these very short waves the resonance points were very broad and the change in degree of scattering as the reflector was moved quite small.

In order to obtain a sensibly pure progressive wave field a tank one metre in length was constructed. Taking Biquard's value of 0.047 for the absorption coefficient of xylol at 7.96 megacycles and reducing this to 4.94 megacycles, the lowest frequency employed, by assuming the absorption coefficient directly proportional to the square of the frequency, its value at this frequency would be about 0.018. Since the crystal was located within a few centimetres of one end of the tank, the intensity of the wave reflected from the far end of the tank would accordingly have fallen to something less than 10^{-3} of that originating at the crystal. The field through which the light passed could thus be regarded as consisting essentially of progressive waves. The same universal mount was used for the crystal as in the case of standing waves.

Measurements of optical intensity of both positive and negative orders from zero to five were carried out in xylol and petroleum ether as a function of ultrasonic intensity at frequencies of 4.06, 4.82 and 5.56 megacycles with standing waves, and at frequencies of 4.94, 5.84 and 6.72 megacycles with progressive waves. The above frequencies corresponded to the 11th, 13th and 15th harmonics of the two crystals. With the power available, ultrasonic intensities giving as high as 10 orders could be obtained, but as indications of cavitation and other disturbances in the liquid began to appear, the measurements were restricted to sound intensities giving rise to five or six orders of measurable intensity. Normally incident light was employed in all cases.

For each frequency a torsion pendulum curve was obtained at the end of the run, one of the electrical methods being used to measure the ultrasonic intensity during the course of the measurements of the diffraction patterns. The reflection coefficient and characteristics of the torsion pendulum were carefully determined so that a calculation of the absolute intensity in watts per cm.^{2} could be effected. In order to ascertain whether or not the standing wave field in the small tank suffered any distortion due to possible reflections from the side walls of the biological cell, the standing wave measurements were repeated in the large tank with a plane glass reflector placed at a distance from the crystal equal to that existing between the crystal and the end of the small tank. Results obtained at a frequency of 4.94 megacycles in the large tank checked those obtained in the small cell at 4.06, 4.82 and 5.56 megacycles to well within the errors of measurement.

Results and Discussion

The theory of Raman and Nath, referred to in the introduction, takes account of both progressive and standing wave fields. In the case of progressive waves the theory predicts the appearance of multiple orders, the frequency of any given order being changed by the Doppler effect of the moving sound waves from ν, the frequency of the incident light, to $\nu+n\nu^*$ for the positive orders and $\nu-n\nu^*$ for the negative orders, n being the number of the order and ν^* the frequency of the ultrasonic disturbance. The intensity of the mth order relative to that of the nth is given by the relation

$$\frac{I_m}{I_n} = \frac{J_m^2(v)}{J_n^2(v)} ,$$

where J_m and J_n are the Bessel's functions of order m and n, and the argument is given by

$$v = \frac{2\pi L \delta n}{\lambda} ,$$

where L is the length of path in the disturbed medium, δn the maximum variation in refractive index, and λ the wave-length of the incident light. From the nature of the Bessel's functions it is evident that, under certain conditions, some orders must fall to intensities much lower than those of orders of higher number.

In the case of standing waves, however, each order, instead of having a single frequency, consists of a series of sub-components of frequencies $\nu \pm 2r\nu^*$ for the even orders and $\nu \pm (2r+1)\nu^*$ for the odd orders, r being a positive integer. Thus, in the case of progressive waves, the light from any two orders should be completely incoherent, whereas, in the standing wave case, any two even orders should be partially coherent, a positive and negative order of a similar number should be completely coherent and any even order should be completely incoherent with any odd order. An experimental study of the coherence relations among the various orders produced in a standing wave field has been made by R. Bär (3). The results bear out the above-mentioned theory exceedingly well.

Very recently L. Ali (1) has made direct measurements of the shift in wave-length of the various orders due to diffraction by progressive waves, and has found quite good agreement with the theory for the latter case. The relative intensity of the $\nu \pm 2r\nu^*$ sub-component in the $2n$th order is given by $J^2_{n-r}(v/2)\, J^2_{n+r}(v/2)$ and that of the $\nu \pm (2r+1)\nu^*$ sub-component in the $(2n+1)$th order by $J^2_{n-r}(v/2)\, J^2_{n+r+1}(v/2)$. The total intensity of the mth order to that of the nth is given by the relation

$$\frac{I_m}{I_n} = \frac{\int_0^{\pi} J_m^2 (v \sin\theta)\, d\theta}{\int_0^{\pi} J_n^2 (v \sin\theta)\, d\theta} ,$$

and may be obtained by summation of the various sub-components in each order.

Variation with Relative Ultrasonic Intensity

In Fig. 1 the results of observations made with the photo-cell in a standing wave field at a frequency of 4.06 megacycles are shown. The liquid employed was petroleum ether. Each graph shows the diffraction pattern for a certain value of the ultrasonic intensity. Light intensities are expressed as actually observed in percentage of the intensity of the incident unscattered beam, rather than in percentage of the most intense order in any pattern as in the graphs shown by Raman and Nath. Since, for constant path length and light wave-length, the parameter v in the above-mentioned theory is directly proportional to δn, the maximum variation in index of refraction, and this is proportional to the square root of ultrasonic intensity, observations of light intensities were made as a function of the latter quantity. This arbitrary scale was reduced to the units of v by the choice of a suitable multiplying factor giving closest agreement between observed and theoretical values of light intensity over the whole range of ultrasonic intensities. The figures in the upper right-hand corner of each graph give the values of v thus obtained. The solid vertical lines represent intensities obtained from the Raman-Nath theory, while the circles represent observed data. The agreement is surprisingly good over the whole range. Careful examination of the theoretical intensities reveals the fact that the decrease in relative intensity with increasing order number is not quite monotonic for the higher

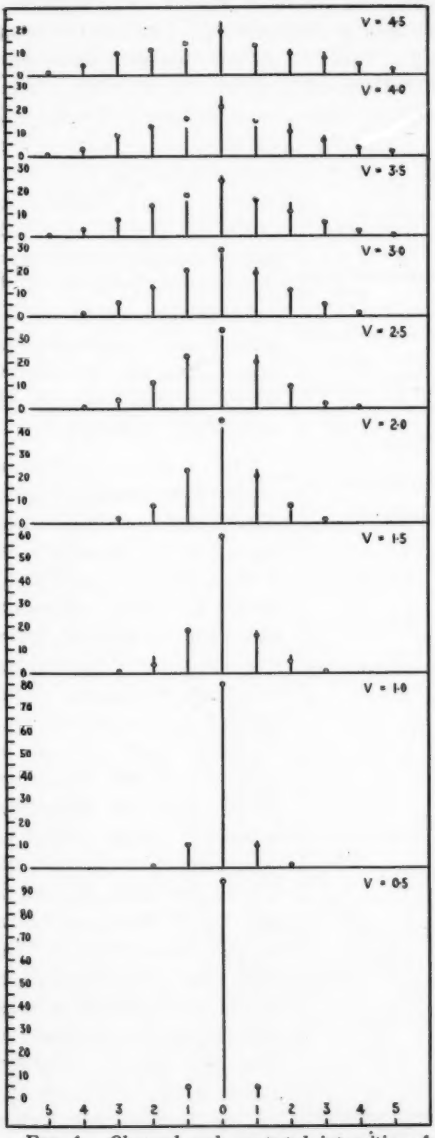


FIG. 1. *Observed and computed intensities of five orders obtained with standing waves. Each graph refers to a single value of the Raman-Nath v. Ordinates—per cent of incident light intensity. Abscissas—positive and negative order numbers.*

values of v, whereas the observed intensities do decrease monotonically. This deviation is undoubtedly due to the imperfections of the actual sound field. Since the ultrasonic beam is slightly divergent and a certain amount of attenuation in the liquid exists, the actual sound field is not quite the ideal rectangular prism of plane waves postulated in the theory. At the higher values of v a certain lack of symmetry in the intensities of positive and negative orders is noticeable. This assymetry persisted in all the measurements and appeared to be due to some type of distortion in the field. While it was possible to produce a very marked lack of symmetry by setting the crystal, reflector and light beam out of parallelism, under no conditions was it possible to obtain complete symmetry at all ultrasonic intensities.

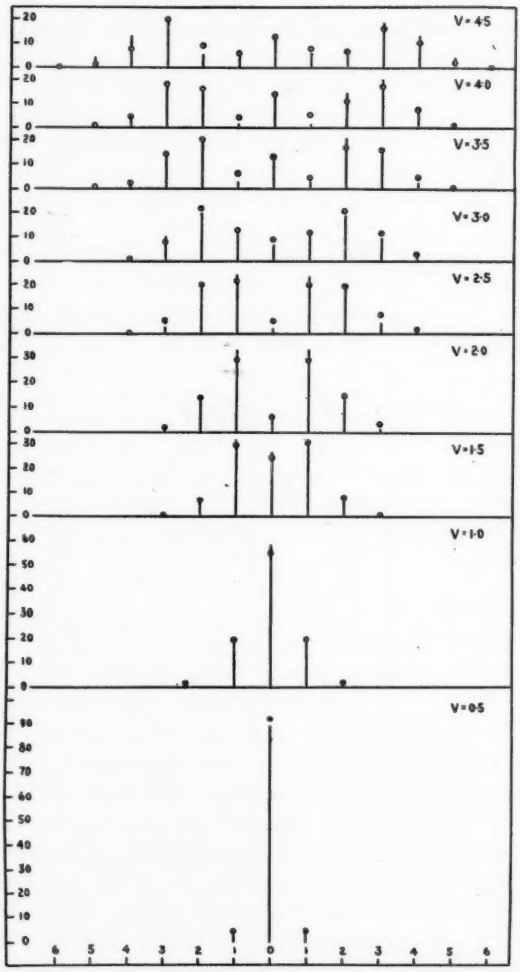


FIG. 2. *Observed and computed intensities of five orders obtained with progressive waves. Each graph refers to a single value of the Raman-Nath v.*
Ordinates—per cent of incident light intensity.
Abscissas—positive and negative order numbers.

Fig. 2 shows a similar set of data obtained with xylol, using progressive waves, at a frequency of 4.94 megacycles. As before, the solid lines represent intensities computed from the theory and the circles the observed values. The difference in nature of the patterns produced in a progressive wave field from those due to standing waves is quite striking. The central order falls to a very low value at $v=2.5$ and later increases to a second maximum. The first order goes through a similar cycle and the second has begun to decrease in intensity at the highest value of v. The choice of the multiplying factor converting square root of ultrasonic intensity to the units of v is considerably

simplified in the case of progressive waves, since it is necessary only to compare the observed ultrasonic intensities at which the central order attains its minimum and maximum values with the corresponding values of v obtained from the theory. A slight lack of symmetry is again observable at the higher values of v and could not apparently be eliminated.

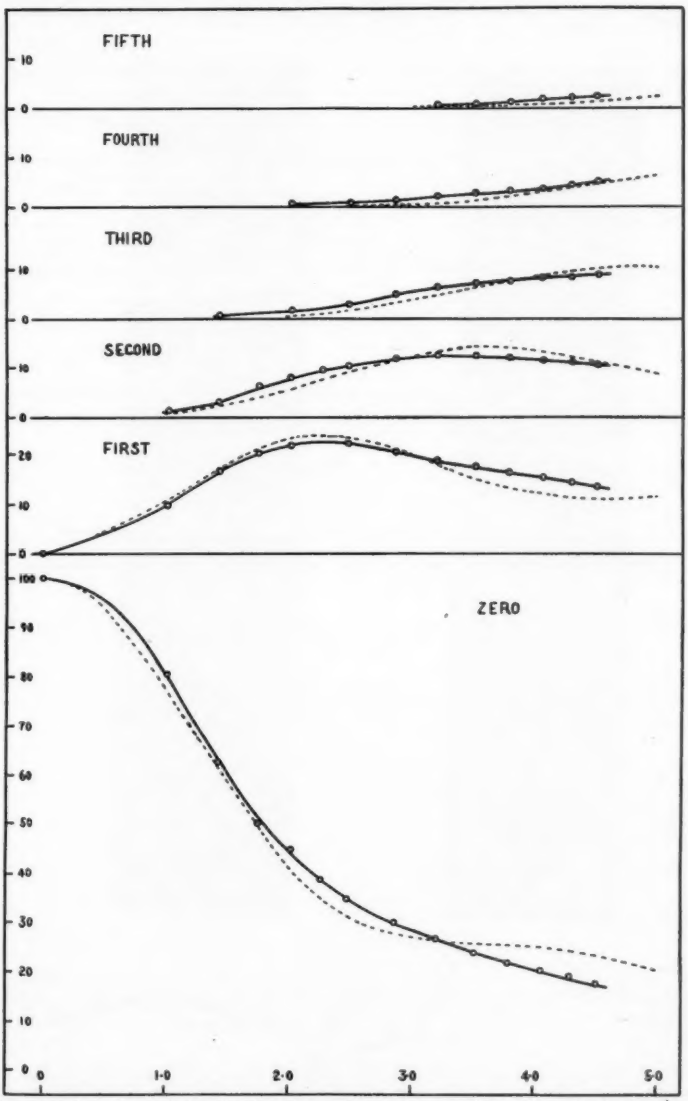


FIG. 3. *Continuous variation in light intensity with increasing values of the Raman-Nath v for a standing wave field. Each graph refers to a single order.*
Ordinates—per cent of incident light intensity.
Abscissas—Raman-Nath v values.

Figs. 3 and 4 show the progressive variation in intensity of the various orders with increasing values of v for standing and progressive waves respectively. The dotted lines represent theoretical values of light intensity, while the solid curves through the circles represent the mean value of each pair of positive and negative orders observed.

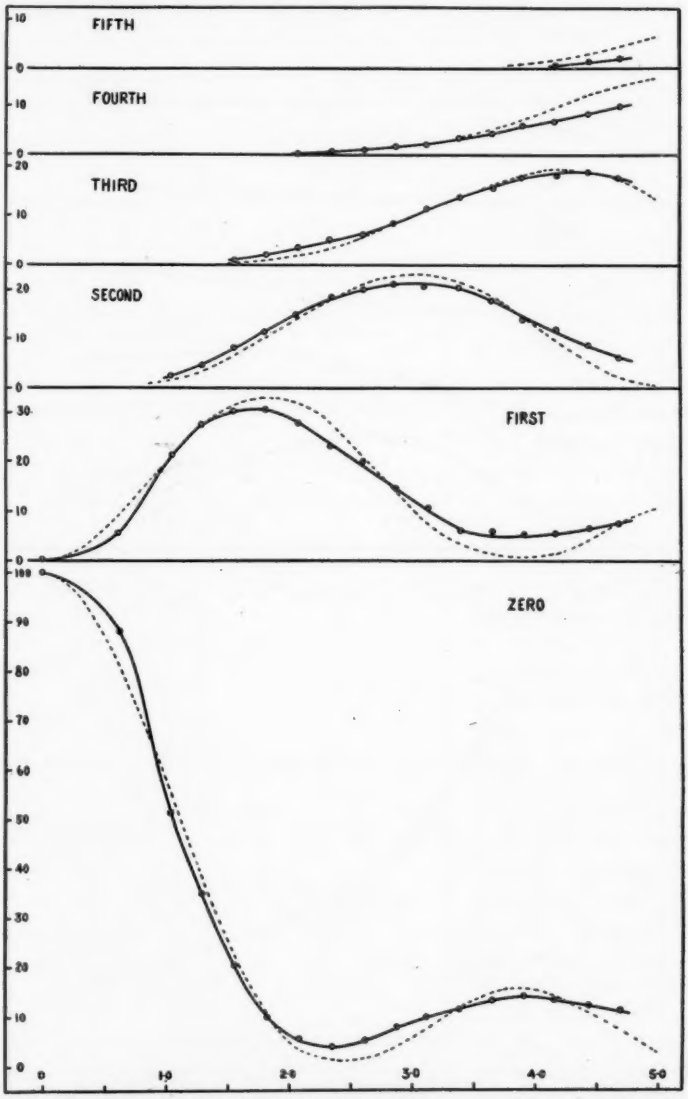
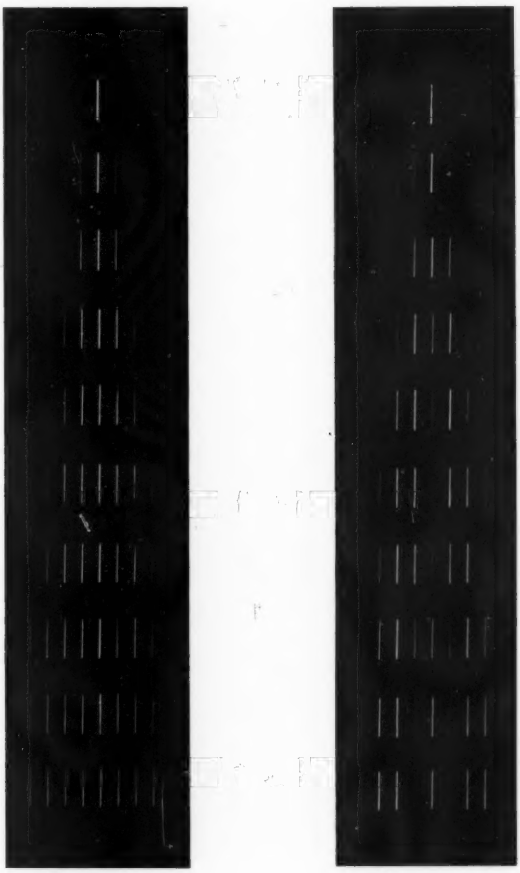


FIG. 4. *Continuous variation in light intensity with increasing values of the Raman-Nath v for a progressive wave field. Each graph refers to a single order.*
Ordinates—per cent of incident light intensity.
Abscissas—Raman-Nath v values.

PLATE I



a *b*

FIG. 5. *Photographs of diffraction patterns, (a) standing waves, (b) progressive waves. Exposures made at ten ultrasonic intensities corresponding to values of v ranging from 0 to approximately 4.0 in equal steps.*

The frequencies at which these observations were made are respectively the same as those of Figs. 1 and 2. The observed curves, because of the imperfections of the actual sound fields, have lower maxima and higher minima than those computed, but the general agreement is extremely good.

Similar curves were obtained at frequencies of 4.82, 4.94 and 5.56 megacycles with standing waves and at 5.84 and 6.72 megacycles with progressive waves. The agreement with the theory was equally satisfactory in all cases.

Fig. 5 shows two photographs, each consisting of 10 exposures, (*a*) of the standing and (*b*) of the progressive wave patterns. Exposure times were so estimated from the intensity values obtained with the photo-cell as to give approximately the same intensity to the most intense order in each pattern for all the exposures. The exposures were made for values of v from zero to about 4.0 advancing in steps of approximately 0.45. Comparison of the progressive wave patterns with the graphs shown by Raman and Nath for the above values of v shows a very satisfactory qualitative agreement.

Absolute Measurements

From the constants and deflections of the torsion pendulum, some approximate determinations of the absolute energies involved were made for the standing wave field in petroleum ether. The velocity of sound in this liquid, its density and index of refraction, were determined experimentally. With this information it was possible to determine the energy density in watts per cm.^{2} and consequently the maximum variation in index of refraction. Knowing the length of path in the disturbed medium and the wave-length of the light used, it was possible to evaluate the quantity v. The quantities used were as follows: velocity, 1.15×10^5 cm./sec.; density, 0.633; index of refraction, 1.365; length of path, 2.3 cm.; light wave-length, 5.89×10^{-5} cm. Table I shows the nature of the agreement between the computed values of v and those for which the observed light intensities gave closest agreement with the theory.

TABLE I

Frequency, megacycles	Energy density, watts/cm.^{2}	Maximum variation in refractive index	v, from torsion pendulum data	v, observed
4.06	0.171	1.34×10^{-5}	3.29	4.50
4.82	0.106	1.05×10^{-5}	2.58	4.00
5.56	0.183	1.38×10^{-5}	3.40	4.20

In view of the inaccuracies of absolute measurements at these frequencies the agreement is quite satisfactory.

Number of Orders Visible as a Measure of Ultrasonic Intensity

While investigating the effect of ultrasonic intensity on the degree of diffraction, it appeared of interest to determine the manner in which the number of orders visible in the diffraction pattern of a standing wave field varies with ultrasonic intensity. R. Wyss (18) has made use of the number

of orders visible when a light beam is passed through a sound field at varying distances from the source, to measure the relative absorbing powers of various liquids. By means of an arbitrary scale of visually estimated intensities Wyss was able to obtain quite smooth curves showing the relative absorbing powers of ethyl alcohol, amyl alcohol, benzene, xylol and carbon disulphide.

Since it is difficult to define a threshold of visibility, certain arbitrary levels of light intensity were chosen in the writer's experiments as indicated by the deflections of the galvanometer measuring the intensities of the various orders. These levels corresponded to intensities of 0.57 and 0.86% of that of the unscattered beam. Fig. 6 shows two curves giving the number of

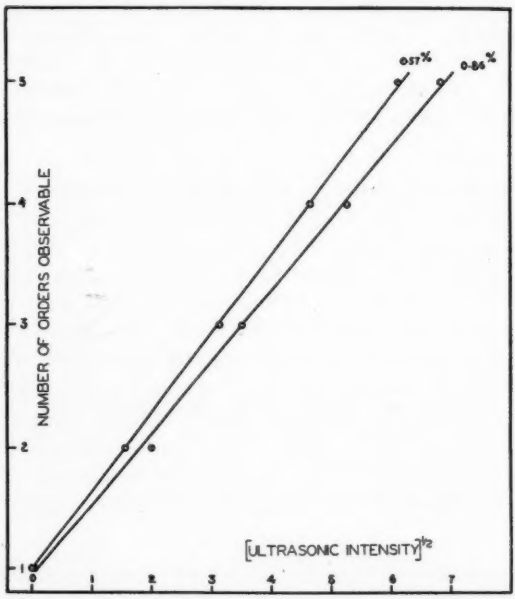


FIG. 6. *Number of orders having intensities equal to or greater than 0.57% and 0.86% respectively of the intensity of the incident light, as a function of ultrasonic amplitude.*

orders having an intensity equal to or greater than these arbitrary levels as a function of the square root of ultrasonic intensity. Each point was obtained by setting the photo-cell on the given order and determining the ultrasonic intensity for which the galvanometer gave the required deflection. It is evident that the number of orders observable, at least for orders up to five, is very closely a linear function of the square root of ultrasonic intensity and hence of ultrasonic amplitude. Examination of Raman and Nath's theory indicates that this relation is to be expected.

Knowing the above relation it is possible to evaluate the absorption coefficients of the liquids studied by Wyss. The natural logarithm of the ultrasonic amplitude plotted as a function of distance in centimetres should

give a straight line of slope equal to the absorption coefficient. Actually the only liquid for which Wyss' results give a good straight line is benzene; the two alcohols and xylol give curves having a slight upward concavity while the carbon disulphide curve shows a slight downward concavity. Taking the slope of the best straight line through each of the above curves, the values in Table II were obtained for the respective absorption coefficients at the frequency of 6.0 megacycles used by Wyss.

TABLE II

Liquid	Ethyl alcohol	Amyl alcohol	Xylol	Benzene	Carbon disulphide
Absorption coefficient	0.057	0.069	0.071	0.33	4.3

Of the liquids listed in Table II, benzene and xylol have been studied by Biquard (6, 7) who used a frequency of 7.96 megacycles. If Biquard's values are converted from 7.96 to 6.00 megacycles, and it is assumed that the absorption coefficient is proportional to the square of the frequency, the values obtained are 0.027 for xylol and 0.33 for benzene. The very close agreement between the two values for benzene is undoubtedly fortuitous, but the order of magnitude in both liquids is correct and serves to corroborate the abnormally high values of absorption coefficient reported at these frequencies. R. Bär (2) has already drawn attention to the excessively high absorption in carbon disulphide. A more complete study of absorption coefficients at various frequencies has been made by Biquard (8), but the writer has not yet been able to obtain a copy of the work.

Effect of Light Wave-length

According to the theory of Raman and Nath, the quantity v determining the degree of scattering is inversely proportional to light wave-length. Hence the effect of increasing the light wave-length should be equivalent to that obtained by decreasing the square root of ultrasonic intensity. A few measurements were conducted in a standing wave field with light of the wave-lengths 436, 546 and 589 millimicrons. An appreciable flattening of the diffraction patterns with decreasing wave-length was noted, but the range studied was too limited to give good quantitative agreement with the theory. It is hoped to conduct some further studies of this phase of the problem with both standing and progressive wave fields over a considerably larger range of wave-lengths.

Conclusion

From the results of the foregoing experiments it is evident that the theory proposed by Raman and Nath gives the correct type of envelope for the diffraction pattern produced by both standing and progressive wave fields in the frequency region investigated. The results of Bär and Ali regarding the spectral characteristics of the diffracted light appear further to substantiate this theory.

Bär (4) has, however, recently reported on some apparent discrepancies observed in the region of 7.5 megacycles. While the nature of the intensity distribution in the various orders observed by Bär appears to be in good qualitative agreement with the Raman-Nath theory, experiments carried out with the incident light inclined slightly to the planes of the sound waves give results that are not in accord with the above theory. In addition, Bär was able to obtain "photographs" of the actual ultrasonic grating by inserting a photographic plate or strip of sensitized paper in an appropriate position in the light beam just behind the stationary sound field, no lens system of any type being required to focus the light on the plate. From these observations it is apparent that the light rays in passing through the sound field undergo not only changes in phase, as assumed by Raman and Nath, but also some changes in amplitude as postulated by Lucas and Biquard. Bär notes that these discrepancies are considerably more apparent at a frequency of 7.5 megacycles than at 1.5 megacycles. Hence he concludes that Raman and Nath's assumption of phase changes alone is not justified, particularly at the higher frequency.

Since the writer's quantitative measurements demonstrate the validity of the Raman-Nath intensity distribution for frequencies ranging from 4 to 7 megacycles, there appears at first to be a contradiction in the experimental results. It seems possible, however, that these apparent anomalies may be explained as follows:

In the theory proposed by Raman and Nath, the type of sound field postulated is a rectangular prism of plane waves progressing in a direction normal to that of the incident light, the amplitude of the variation in refractive index at any instant being constant across the field in the direction of motion of the light rays. A single light ray is hence incident normally on a medium of constant refractive index. Under such a condition the light can suffer changes in phase only, and the Raman-Nath assumption is quite valid. The sound field produced by an oscillating crystal, however, is not quite of this ideal form. It is well known that the intensity distribution across the ultrasonic beam is by no means constant, while there is certainly not a plane surface of discontinuity at the edge of the field. Consequently a light ray, even though incident in a direction normal to the axis of the ultrasonic beam, will suffer some refraction on entering the sound field. Once bent, the ray will be passing through layers of varying refractive index and will suffer changes in amplitude as well as in phase. If such is the case, the rays may eventually come to a focus, producing the fringes observed by Bär and others. Furthermore, the Raman-Nath theory for oblique incidence, which is dependent on the existence of a rectangular sound field, will not be valid. In the case of normally incident light, however, it is quite conceivable that small changes in amplitude, combined with changes in phase of the light rays progressing through the liquid, will give rise to an emergent light wave surface that approximates very closely to that which would be produced if changes in phase alone occurred. That such is the case seems to be borne out by the

close agreement between the observed envelopes of the diffraction patterns and those predicted by the Raman-Nath theory. Bär's observations of the fact that the discrepancies noted at 1.5 megacycles are much smaller than those at 7.5 megacycles seem to lend support to the above hypothesis, since the longer the sound wave-length the higher the probability of the light entering under the conditions postulated by the theory.

It would thus appear that while Raman and Nath's fundamental assumption is not entirely true for a practical sound field, the nature of the emergent light wave surface is very much that which would obtain if changes in phase alone occurred, so that the intensity distribution in the various orders of the diffraction spectrum is very closely that predicted by the above theory. From the results of Bär and the writer, it would appear that this is true for frequencies ranging from 1.5 to 7.5 megacycles. Until a theory can be developed which will take complete account of the true nature of a practical sound field, it would appear that the theory of Raman and Nath approximates most closely to the observed diffraction effects.

Acknowledgments

In conclusion the writer wishes to express his indebtedness to Mr. G. S. Field for many helpful suggestions regarding the experimental technique, and to Dr. L. E. Howlett for many valuable discussions of the theoretical aspects of the problem.

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MICROSCOPIC FEATURES OF CERTAIN ALBERTA COALS[1]

BY I. W. JONES[2]

Abstract

Microscopic examination of Alberta coals shows that they are composed principally of materials derived from the woody parts of plants. Many woody structures are visible in thin sections and on polished and etched surfaces. Spores are present in the coals, but are relatively few in number. The resin content varies considerably, attaining a high proportion in the cannel coals of the Crowsnest Pass region in British Columbia, bordering the southwestern part of Alberta. The correlation of seams in the Alberta coal deposits on the basis of their microscopical characters has not yet proved to be feasible. A wide field is open here for palaeobotanical research on the nature and classification of the plant structures visible in these coals by means of the microscope. The investigation described here may be considered as being relatively only a beginning to further work that should be done in the study of the microscopical features of Alberta coals by the geologist, chemist and botanist.

Introduction

There are in Alberta three main coal-bearing formations: the Kootenay, the Belly River or Saunders, and the Edmonton formations. The Kootenay formation is Lower Cretaceous in age and the two others are Upper Cretaceous. Within each of the formations there are several coal seams. Coals of Tertiary age, which are abundant farther east in Saskatchewan, are found also in Alberta, but their occurrences are few and of minor importance.

The Kootenay formation occurs in the western part of the province in long belts between the easterly ranges and along the eastern front of the Rocky Mountains. The coal seams of this horizon are generally much folded and faulted. The second coal horizon, the Belly River formation, is found along the borders of the broad synclinal trough that forms the central part of Alberta, *i.e.*, the Belly River coals are found in the foothills in a complicated series of folds, and along the southern and eastern part of the province in almost flat-lying beds. The Edmonton formation has a somewhat similar distribution, occurring along the outer areas of the foothills, being buried under younger sedimentary rocks in the trough, and reappearing as almost horizontal beds on the east side of the broad syncline (see Fig. 1).

The quality of the coals is largely dependent on their relative position with respect to the mountain uplift. The coals become lower in rank from west to east. The Kootenay coals in the mountains are high-grade bituminous; as a rule, they are good or fair coking types, and, in a few regions of intense

[1] *Manuscript received June 15, 1936.*

This paper deals with a phase of a more extensive investigation of Alberta coals on which a thesis was presented as part of the requirements for the degree of Doctor of Philosophy at the University of Toronto, 1928.

[2] *Geologist, Bureau of Mines, Quebec. Holder, at the time, of a bursary under the National Research Council of Canada.*

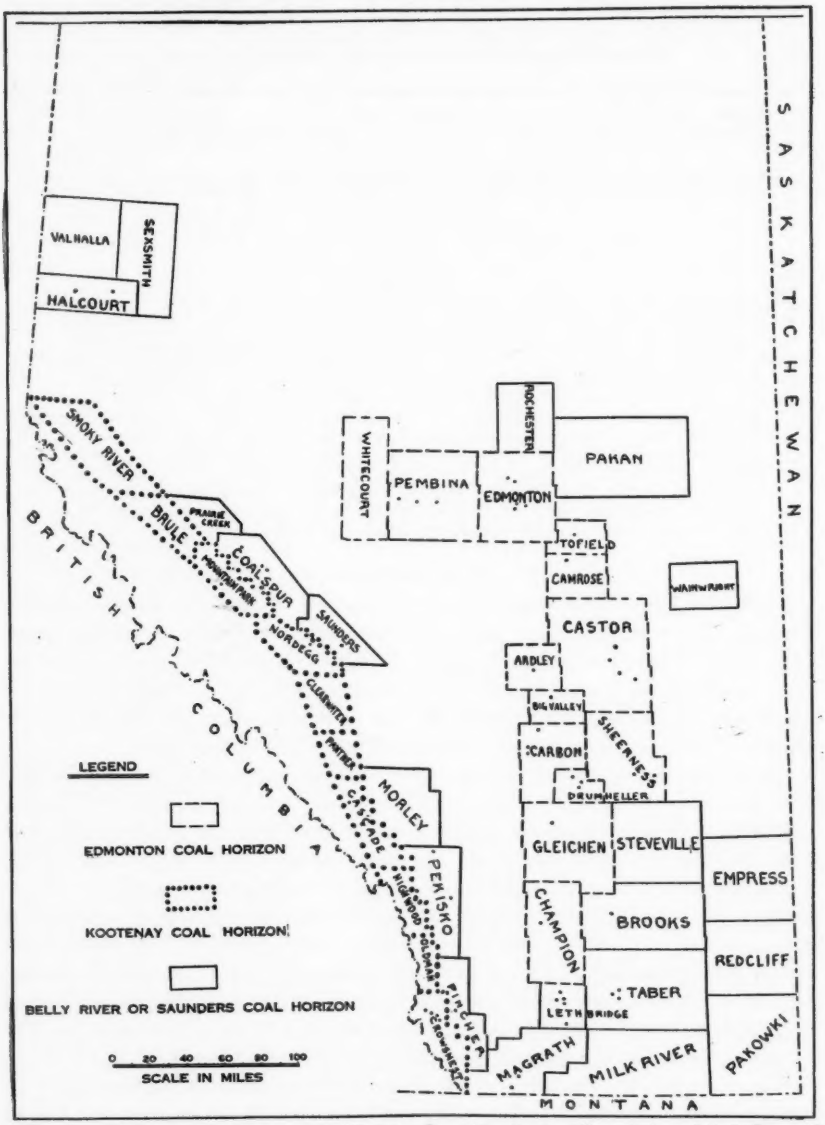

FIG. 1. *Coal areas of Alberta. Modified from map by J. A. Allan, Sci. and Ind. Research Council of Alberta, 1924.*

pressure, semianthracites are found. The Belly River and Edmonton coals vary from low-moisture sub-bituminous in the foothills to higher-moisture black lignites farther east, and to brown lignites still farther from the mountains. The lowest rank of coal is found in the Tertiary formations of southern Saskatchewan.

The coals of Alberta, having a widespread occurrence and varying greatly in character—although belonging to the same general (Cretaceous) age—offer a wide field peculiarly favorable to many years of fruitful and varied research. The microscopical nature of the coals, the study of which formed a major phase of the writer's investigations of four years' duration, is in itself a subject capable of almost endless study. This paper describes some of the results obtained from studies of Upper Cretaceous (Edmonton) coals, chiefly from the Drumheller area, and of coals of Lower Cretaceous (Kootenay) age from some of the foothill and mountain areas of the province. It is hoped that, in addition to recording the results already obtained, this paper will draw attention to the large amount of research of this type that yet remains to be done in the several other areas and on the many other coal seams of the province not dealt with in this investigation.

Methods Employed

It was found, after many repeated attempts, that Alberta coals are not amenable to the making of thin, transparent sections, as they are impregnated with a dark, almost opaque substance. In order to obtain any degree of transparency, the sections must be much thinner than those ordinarily required for coals such as are found in the Palaeozoic formations of America and Europe. It was found, furthermore, that, even in the few apparently thin sections obtained, the structural features of the various constituents were only poorly revealed, whereas on polished and etched surfaces of the same coals, these features were clearly visible under the microscope. The method employed in making thin sections of Alberta coals, with the necessary precautions taken in the procedure, is included in the original manuscript (4) dealing in greater length with the whole investigation. As the method of studying polished and etched surfaces by reflected light was found to be satisfactory, both in the results obtained and in speed of operation, only this method is described in this paper.

The procedure followed in preparing surfaces of Alberta coals involved two stages—polishing and etching. At first considerable difficulty was encountered when it was endeavored to obtain a smooth, bright surface. The coal would crack and break away on the surface as small scales, owing to the high moisture content of the coal. The absorption of more water during the operations caused swelling, even though the specimen had been soaked in paraffin. To offset this difficulty, the coal specimens were heated and soaked in a shellac solution. It was found that they would then take a good polish, and water could be used during the operations without fear of producing cracks or scaling.

In detail, the procedure was as follows:

The piece of coal was cut to the desired size by use of a hacksaw. As large a piece as can be polished may be cut. The specimen was completely immersed in an alcohol solution of shellac, and allowed to soak for a few hours at room temperature, or sometimes in an oven at about 40° C. After drying, the

surface to be studied was ground on a revolving cast-iron disc with No. 90 alundum powder as an abrasive. This gave a roughly level surface. A smoother, flat surface was obtained by grinding on another cast-iron disc with No. 200 alundum powder. The specimens were then washed and placed, smooth face downwards, in a shallow dish containing shellac solution so that about one inch of coal was immersed. The dish was placed in the oven and the temperature was maintained at about 60° C. for two to three hours, care being taken that the length of time and degree of heat did not cause splitting of the specimen. The coal should by then have been saturated with shellac for a short distance in from the flat surface. After drying, the surface was then ready for polishing.

In polishing, the surface was first rubbed on a thick plate glass with 60-minute carborundum powder and water. The final polishing was done by methods similar to those employed in making polished ore specimens. Rotating wooden discs covered with linen were used. The coverings of the discs and the polishing powders used were as follows: first disc, "medium" Irish linen and alundum lens-finishing powder; second, fine Irish linen and rouge; third, blue English broadcloth and tin oxide. Water was used with the powders throughout. Green billiard cloth on the last wheel is sometimes used in metallographic polishing, but it was found to be inferior to the broadcloth for obtaining a smooth polish on a coal surface. The polished surface was examined under the microscope and any structures visible were noted. As a rule only few structures, those of charred woody constituents, were visible at this stage.

To etch these polished surfaces, a modification of Seyler's method (10) was employed. The etching solution was prepared by adding 10 cc. of concentrated sulphuric acid to 30 cc. of saturated chromic acid solution. Enough water was added to dissolve any chromic oxide that may have precipitated. The liquid was then brought to boiling over a Bunsen burner and allowed to boil until chromic oxide crystals began to precipitate. The polished surface was then immersed in the boiling liquid for about 20 to 45 sec., the lignites requiring the lesser time (Seyler found that from three to five minutes were required for anthracites). This procedure gave an etched surface on which the constituents showed up clearly under the microscope.

The etched surfaces were studied with a metallographic microscope, with vertical illumination from a carbon arc. For obtaining photomicrographs the usual method of photographing polished surfaces was followed. It was found that the time of exposure in the camera was about twice the period necessary for polished surfaces of metals or ores.

The metallographic method of studying coals offers several advantages over that of thin-sectioning. It is applicable to all kinds of coal and is quick and easy. Fairly large surfaces may be examined and the progressive changes in structure may be followed. This method shows the presence of structure as well as the thinnest of sections. Polished surfaces are in reality sections of infinitesimal thinness, and it is possible when examining them to use high

magnifications and to bring out detail that would otherwise escape notice. For the study of woody tissues the polished surfaces are distinctly superior to thin sections.

The polished surfaces show a black and white image, while in thin sections the various components show brown, yellow, and black colors. Investigators experienced in studying sections through transmitted light would probably find it difficult to adjust themselves to the results obtained by reflected light. The greater amount of detailed structure made visible by the latter method, however, would warrant the further study of polished surfaces. To the palaeobotanist, this method opens a wide field for investigating plant remains, as there is revealed in the case of coal an abundance of information that is unobtainable by the usual method of studying individual fossil plant remains that are found associated with sedimentary rocks.

The Components Visible in Alberta Coals

Macroscopic Components

Alberta coals, in common with coals of other parts of the world, are typically laminated, with light and dull bands. The bright bands are composed of definite components of woody parts of plants, stems, or roots. The dull bands are composed of general debris derived from a variety of plant products, and correspond to the general debris of peat deposits. A third type of coal is the mineral charcoal that occurs as thin sheets on the bedding planes and as fragments in the dull bands. These three constituents, visible in hand specimens, are known respectively as "anthraxylon", "attritus", and "fusain" (12, 13).

The differentiation between dull and bright bands is more sharply defined in the Kootenay and Belly River coals of Alberta than in those of the Edmonton horizon. In the later coals the banding may be more accurately described as "bright" and "duller", for there is in most cases no truly dull coal. The duller bands of the Edmonton coals have more or less a silky lustre and have a large percentage of wood debris. Fusain is common in all the coals, but possibly more so in the older ones. In the Edmonton formation, however, the Ardley seam is characterized by having a larger percentage of fusain than the other seams of that horizon.

The Microscopic Components

Anthraxylon

Almost all the Alberta coals are of the xyloid or anthraxylous type, and the microscope reveals a preponderance of woody structures. The bright bands in the specimens examined always showed cellular structure after etching, with the cell walls showing various stages of decomposition and metamorphism. In some cases the cell walls have been flattened by pressure and the cell cavities are almost invisible. A much compressed piece of wood is illustrated in Fig. 2; the cell walls are almost touching. Fig. 8 shows a portion of a bright lens with cellular structure in a better state of preservation. The same illustration shows that various states of preservation may obtain in the

same lens, the central band of the wood in this case being much decomposed. It was found that these lenses of bright coal showing advanced stages of decomposition under the microscope characteristically possess a rather silky lustre in the hand specimen, while those bands with well preserved cellular structure have a lustre more brilliantly glossy.

Woody structures are also found in the duller bands, and sometimes they make up a large percentage of these bands. These woody fragments may occur as thin lenticles or streaks, or as minute fragments, both embedded in the dull, dense groundmass. The former are usually visible to the naked eye. Figs. 3 and 7 show closely packed, laminated bright and dull streaks. Various minute bodies from the woody parts of plants are often well preserved in the dull zones, corticular tissues being common (Fig. 4).

Fusain

The structure of woody parts of plants is best preserved in the charred fragments. Several such structures have been found in the Alberta coals (see Figs. 5, 6, 9). The charred vegetable matter often forms thin "partings" between the bedding planes of the coals, and many horizontal surfaces will show this thin, carbonized film. Charred fragments are also found embedded in the dull groundmass, and the small, well defined structures in Fig. 4 probably owe much of their distinctness to their having been at least partly charred. Many very delicate structures have been preserved as a result of the plant tissues having been converted to fusain (Fig. 5).

Two explanations of the origin of fusain are prevalent. Jeffrey (3) supports the theory that forest fires occurred on the land adjacent to the basin of deposition, and the charred fragments were washed out over the swamp. White (14) believes that the fusain "may be regarded as representing undecayed or partly decayed plant debris lying on the surface at times of exposure of the peat by evaporation of the water cover". This explanation is probably the more acceptable and would account for most of the fusain occurrences in Alberta. A third possible explanation may be offered, however, to explain some occurrences of this material. Fusain was found to be abundant in the impure bands of coal, especially in "bone" layers, surrounded by mineral matter. If this abundance of mineral matter represents a deepening of the water cover and an influx of sediments, temporary exposure under the conditions mentioned by White could not be offered as an explanation. It is possible that this fusain may result from the action of alkaline solution either present in the water of the original peat swamp or derived from mineral matter enclosing the fragments of fusain. The alkaline solutions, by dissolving certain substances from the woody material, would leave a residue richer in carbon. The delicate nature of several of the preserved plant tissues does not favor the thought that the fragments were transported with the sediments. Pishel (8, p. 176) observed a similar abundance of mineral charcoal associated with impure coals. The action of alkaline solutions derived from mineral matter may also have a bearing on the origin of some of the fusain fragments found embedded in dull coal, which usually carries the higher

percentage of ash. Furthermore, the conversion to fusain seems to have progressed selectively; some portions of a woody fragment are charred while others are not. In general, it appears that corticular tissues have been converted to fusain in Alberta coals. In experiments with alkaline solutions a similar selective effect was observed, the bark of elm being more readily affected by the solutions than the wood of the same tree.

Dull Coal, or Attritus

In the dull coal, or attritus, are to be found the components representing the general debris of the original swamp or forest growth. These laminae in Alberta coals are not so typically dull in lustre as in the older coals described by other investigators. A large portion of the dull bands of the Cretaceous coals is composed of a groundmass that has originated from extreme decomposition and "gelification" of woody plants. As a result, these layers may be more accurately described as possessing a silky lustre. In the groundmass are embedded small fragments of partly decayed wood (anthraxylon chips and fusain), which have already been described. These fragments usually constitute a large proportion of the duller layers, and few other plant entities are visible. In some cases spores, pollen grains, and resin grains have been observed.

The number of spores present is relatively small when compared to the spore content in Carboniferous coals of other regions. This is to be expected, since by Cretaceous time the spore-bearing plants had been largely supplanted by the higher types of vegetation. The spores are present, however, in greater number than might have been expected. Almost every etched surface or thin section of dull coal contained a few spores. In etched surfaces the spore cases were not clearly outlined. In all the few thin sections that were successfully made of these coals, spores were present and were the first objects, and often the only ones, to become transparent (Fig. 13). The spore content of the Alberta coals examined, however, does not appear to be of sufficient abundance to affect the chemical character of the coals. No typical spore-coal has been found in this province.

Pollen grains are present in these Cretaceous coals, but do not seem to be as numerous as might be expected. This apparent absence may be due in part to inability of the writer to recognize these bodies. Pollen grains appear to be more common in the higher seams of the Edmonton formation than elsewhere.

Resin grains are relatively abundant. Often the only sign of former lignified tissues is the presence of numerous resin particles that represent former cell fillings (Fig. 12). Resin is found in the cells of the bright woody coals. Also, numerous grains of various sizes are found embedded in the dull groundmass. The presence of these resin particles in the groundmass contributes largely to the silky or resinous lustre. Resin forms an important constituent of western Canadian coals and its presence or absence affects the chemical properties of the coals. An extreme case of high resin content occurs in the cannel coals of the Crowsnest Pass region in southeastern British Columbia;

in some specimens from near Michel, B.C., resin particles were found to constitute as much as 75% of the mass. These coals have the appearance and chemical properties of cannel coal, and may correctly be termed as such even though the typical cannel coals of Palaeozoic age owe their character to a high content of spores. The "grey" coal at Brule also owes its character to the preponderance of resin. Examination of the coals would indicate that resin is more abundant in the Kootenay coals than in those of later age.

Leaf cuticles are present to some extent. As a rule there is some difficulty in distinguishing between spores and cuticles. In well defined examples, however, a cuticle wall displays a serrated inner edge where the underlying epidermal cells formerly existed. The spore wall, on the other hand, has a smooth inner side and is often serrated along the outer edge. The long, slender streaks in Fig. 10 are probably leaf cuticles.

Fragments of cell walls are abundantly present in the dull layers of these Cretaceous coals. Portions of seeds have also been doubtfully recognized.

Certain Upper Cretaceous Coals of Alberta

General Statement

The upper Cretaceous coals of Edmonton age were the first to be examined in this study, as the area where these coals chiefly occur is easy of access and the geologic relations of the various seams have been rather thoroughly established by previous field investigations.

The coals of the Edmonton formation are mined in a belt extending in a north-south direction in the central portion of the province. The formation

TABLE I

Section of Edmonton formation in Red Deer Valley

Feet	Description	Feet	Description
	Contact overlain disconformably by Paskapoo formation (Tertiary)	15	Rock
		2	No. 8 seam
60	Sandstone and shale	100	Rock
20	No. 14 (Ardley) seam	4	No. 7 seam
50	Rock	25	Rock
3	No. 13 (Nevis) seam	2	No. 6 seam
170	Rock	70	Rock
1	Volcanic tuff	5	No. 5 seam
50	Rock	15	Rock
5	No. 12 (Thompson) seam	1	No. 4 seam
90	Rock	10	Rock
6	No. 11 (Carbon) seam	1	No. 3 seam
155	Rock	10	Rock
3	Corbicula zone	3	No. 2 seam
20	Rock	30	Rock
3	Ostrea zone	6	No. 1 seam
85	Rock	40	Rock
	Ornithominus zone, 110 ft. above No. 9 seam	1	No. 0 seam
		100	Rock
2	No. 10 (Marker) seam		Bearpaw shales at base
60	Rock		
1	No. 9 seam	1,224	Total thickness of Edmonton formation

consists essentially of sandstones, bentonite, clay, soft and indurated shales, nodular shales, ironstone bands, carbonaceous shales and coal. The beds are lying nearly flat, there being in general a west-southwesterly dip of seldom more than 20 ft. to the mile. A description of a generalized section of the Edmonton formation as exposed in the valley of the Red Deer River (2) is given in Table I.

Of the seams listed in Table I, a detailed microscopic examination was made of Nos. 1, 2, 5, 7 and 14.

Coals of the Drumheller Area

Introductory Statement

The Drumheller coal field is situated along the Red Deer River, 85 miles east-northeast from Calgary and 180 miles south from Edmonton (Fig. 1). There are four workable seams in the area, namely, Nos. 1, 2, 5 and 7 of the previously mentioned stratigraphic section. The seams stratigraphically higher than these coals occur in the region to the north and west. Mines extracting coal from the Drumheller seams occur in the valley of the Red Deer River for a distance of about 15 miles. At the time of this investigation, No. 1 seam was worked at various points throughout this distance, No. 2 only in the eastern part, No. 5 mostly in the central, and No. 7 had been mined at one time in the northern part of the area. The mines are entered by adits, slopes and shallow shafts.

The geology of the Drumheller area has been described in detail by Allan (1).

The data in the description of the physical character of the seams were obtained by personal study in the area, but the descriptions given by Allan have also been freely drawn upon. Only the workable seams are described.

No. 1 Seam

Detailed examination of No. 1 seam has been made from samples, taken 6 in. apart, from the Monarch, Midland, Rosedale, and Rosedeer mines. Samples from the top, middle and bottom portions of the seam at the Star and Western Commercial mines were examined.

No. 1 is the thickest and stratigraphically the lowest of the workable seams in the area. It averages from 6 to 7 ft. in thickness. The seam is exposed on the banks of the river in the eastern part of the area, but at the Monarch mine at the western end it is at a depth of 173 ft. The most characteristic feature of No. 1 seam is its division into two benches by a band of bentonite varying from a fraction of an inch to 20 in. Sometimes a band of bone (very impure coal or carbonaceous sediment) accompanies the bentonite, and at other times the bone alone is present. Where this parting is thickest only the top bench (5 to 6.3 ft.) is extracted, but in some mines the whole seam is mined. The roof is shale and bentonitic sandstone.

The coal is mediumly bright in lustre when mined, but assumes a dull lustre and disintegrates on exposure to the air. The coal is typically laminated, with bright and mediumly dull layers and small lenses. A pronounced

characteristic of No. 1 seam is the presence of bands of grey "granular" coal immediately above and below the bentonite parting. So-called "nigger heads" are also common in the eastern mines. These two constituents will be described more fully later.

TABLE II

COAL FROM NO. 1 SEAM

Moisture, %	18.3–19.7
Ash, %	5.6–7.3
Volatile matter, %	31.7–31.9
Fixed carbon, %	42.5–43.6
B.T.U.'s per lb.	9,650–9,830
Fuel ratio	1.35

Analyses (11, pp. 55-57) of the coal in No. 1 seam (as mined) give the values shown in Table II.

Microscopically, a striking feature in No. 1 seam is the preponderance of material derived from woody plants. Although the coal is laminated, with bright and dull zones being present to almost an equal extent, the duller bands contain a large quantity of macerated wood fragments in various stages of decay. Resin particles, fragments of cell walls and numerous corticular tissues are imbedded in a comparatively smaller proportion of dull groundmass. In several instances evidence of abundant woody remains at the base of the seam suggests that the early conditions were those of a heavily forested swamp. The duller layers are more common near the upper part of the seam, and they do not contain as much wood or as many resin fragments. A few probable spores are present in many parts of the seam, but these are more numerous towards the upper portion. The plant remains appear to indicate that deeper water cover existed during the last stages of coal formation in the swamp.

Much of the corticular tissue is present in the duller layers as fusain. Typical structures of this kind are shown in Figs. 4 and 15. These tissues appear to have belonged to coniferous trees. A characteristic of some of the corticular tissues in No. 1 seam is the prevalence of a dumb-bell shape, that is, they have a constriction a little to one side of the centre. These are very common in No. 1 seam, and rare in No. 5. Their abundance in the one seam suggests that their shape is an original feature and is not due to compression.

Some fibro-vascular tissues are illustrated in Fig. 4. In one section there were observed some tissues that resemble those pictured by Knowlton (6, fig. 67c, p. 145) to illustrate the fern "Tempskya knowltoni" from the Lower Cretaceous of Montana.

Fig. 13 shows a spore as seen through a thin section. Other similar spores, though smaller, with the prominent ornamentation on the outer walls have been observed. They occur only in No. 1 seam, but are very few in number. The elongated object shown in Fig. 11 is strikingly similar to one observed by Iwasaki (see (15), fig. 5) in Japanese coals of Tertiary age, and by Winter (15, fig. 6) in an Australian boghead coal. The description given by Winter of these objects would apply equally well to the object in Fig. 11: "the unidentified plant entity is formed round a central channel and there are fine cracks passing inward from each end of the shape."

The compact woody nature of No. 1 seam is illustrated in Fig. 7. Fig. 2 shows the contact of bright and dull bands. In the dull bands many smaller fragments of plant debris may be observed.

Silicified Wood in No. 1 Seam

So called "nigger heads" are common in No. 1 seam in the eastern part of the area. An examination was made of these bodies occurring at the Rosedeer mine, and similar bodies were observed in the Rosedale and Western Commercial mines. These masses occur most commonly in the lower bench of the seam, although they are also found near the top of the coal. In shape they are very roughly cylindrical or, more accurately, they are irregular, rectangular blocks. Their average dimensions are, approximately,—length, 15 in.; diameter, 8 in. The masses are extremely hard, heavy, and are almost black. The long axes of the blocks are orientated vertically or obliquely to the bedding planes of the coal. Along the margins of almost every block there occurs a zone of bright unlaminated coal. This zone, varying up to 2 in. in thickness, does not possess the banding of the adjacent coal, and appears to be cutting across the bedding planes of the seam.

When these masses were examined in the mine, it was thought that they were bodies formed by the accumulation of siliceous material, such as fine sand, that had been permeated by carbonaceous matter. The bright bands of the margins appeared to be small dike-like bodies formed by the solidification of fluid hydrocarbons. Allan has described these "nigger heads" as follows: "These masses of hard bone represent the clay, sand and plant material, washed or blown into depressions on the floor of the basin in which the coal was being formed" (1, p. 45).

It is possible that some of the masses originated by the method suggested by Allan. Microscopic examination, however, of all the specimens collected by the writer, revealed that these blocks are silicified tree trunks, although no suggestion of this nature is indicated in the hand specimens. To the naked eye they bear no resemblance to woody masses.

A transverse thin section of this material is shown in Fig. 14. Most of the cell cavities are filled with quartz, while in some cases only partial replacement of the original cell fillings has taken place. The cell walls are for the most part original and unreplaced by silica, although areas occur where these parts also have been replaced. Most of the silica is the common variety of quartz, but chalcedony and opal also are found. The process of silicification appears to have taken place chiefly by infiltration, with a minor amount of replacement (cf. St. John (9)).

The bright coal bands extending along the sides of the silicified fragments were also examined through the microscope. It was discovered that these zones are not structureless. Irregular cellular tissues, much altered during the coalification process, are in evidence, and they appear to represent the bark of the former trees.

It appears that the silicification of the tree trunks took place after deposition of the vegetable material. The presence of the coalified bark would suggest this hypothesis. The cellular nature of the inner wood offered channels for the infiltration of later siliceous waters, and this feature explains why the adjacent coal is not silicified. The smaller fragments of plant debris were probably at a further advanced state of decomposition and did not offer as free a passage to the percolating solutions. There is no evidence to suggest that these silicified logs were transported by streams into open bodies of water. The occurrence of these large, heavy fragments embedded in the finer, coalified vegetable debris would not support such a hypothesis.

These silicified tree trunks have been determined as belonging to the *Cupressinoxylon* group of plants. The presence of annual rings suggests that the climate was at least seasonal.

Grey, Granular Coal

Reference has already been made to the mode of occurrence of this distinct variety of coal in No. 1 seam. This granular coal is fine textured, hard, and a little heavier than the normal coal. A hand specimen of typical grey coal does not present the banding that is characteristic of other portions of the seam. The granular texture and grey appearance are due to the presence of innumerable conchoidal fracture surfaces. This variety of coal shrinks very little on exposure to air, and it does not break as readily as the normal coal during handling. The grey coal is actually of better quality than the other, but on account of its hardness and appearance it has not found favor with the coal consumers. At most of the mines this coal is discarded.

TABLE III

GREY COAL FROM WESTERN COMMERCIAL MINE

Moisture, %	10.3
Volatile matter, %	34.6
Fixed carbon, %	49.0
Ash, %	6.1
B.T.U.'s per lb.	10,670

An analysis of the grey coal (as received) from the Western Commercial mine gives (1, p. 62) the values shown in Table III.

A suggestion that might be offered to explain the peculiar character of this coal would be that it is composed of many individual grains of coal. A polished surface of a piece of the coal, however, shows that there is lamination in very fine bright and dull streaks as much as 1½ in. in length. On a polished surface the coal loses its granular appearance. Allan suggested that "this (granular) texture seems to have been caused by pressure and slight movement on a bed of coal material made up chiefly of plant seeds and soft structured vegetation, possibly grasses and other marsh growth" (1, p. 45). Examination of this coal through the microscope, however, indicates that the types of plants are not noticeably different from those in other parts of the seam. Etching of the surface showed that constituents of woody origin predominate here as elsewhere. There is, however, a marked difference in the state of preservation of the woody tissues. In the grey coal very little cellular tissue is well preserved; the cells have been flattened and the cell walls greatly

decomposed. It appears as though the wood had decomposed to a greater degree than the wood in other parts of the seam, and had been almost completely "gelified".

The granular texture could be explained as being due to the drying of a jelly-like mass. It is characteristic of such masses to exhibit innumerable fractures upon rapid drying, and the many small cubical joint-planes in the grey coal suggest this mode of origin. The bentonite layer occurring between the bands of grey coal could act as a drying agent. The high absorptive powers of the bentonite would permit the withdrawal of much moisture from the adjacent vegetable mass at a time when the peat was yet in a jelly-like state. Two features add strength to this hypothesis. First, the grey coal contains less moisture than the normal coal (compare analyses, Tables II and III), and it is more compact and more resistant to weathering. Second, it was observed that where the bentonite band was absent, as in parts of the Midland and the Monarch mines, the typical grey coal was also absent.

No. 2 Seam

This seam is separated from No. 1 seam by 39 to 50 ft. of shale and sandstone. No. 2 seam has been worked in the Celtic and Sunshine mines on the east side of Rosebud creek, in the eastern part of the area. At these mines the thickness of the seam varied from 22 in. to at least 40 in. Allan states that "the coal when fresh has a dull lustre due to the fact that it consists largely of the amorphous variety of coal. There are irregular lenses of glossy coal" (1, p. 46). In 1927, when the writer visited the area, the Celtic mine had been abandoned and the Sunshine mine had moved its location to the west side of Rosebud Valley. In the new Sunshine mine the seam was observed to be from 36 to 40 in. in thickness, with a sandstone and shale roof, and a shale floor. The physical appearance of the coal at this point differs from that at the former locations of the mines working in this seam. The coal is, on the whole, bright and massive, and only near the bottom were dull layers noticeable. At various parts of the new Sunshine mine, hard, stony "nigger-heads" occur, sometimes passing from floor to roof, and attaining a width of almost three feet. These masses are bordered by bands of apparently structureless coal of a cannelloid or silky lustre. The "nigger-heads" offer difficulties during mining operations, often being resistant to the usual mining tools. Some of these hard masses have to be left in their place and the workings diverted around them.

A typical analysis (11, p. 57) of No. 2 seam (as mined) gives the values shown in Table IV.

TABLE IV

COAL FROM NO. 2 SEAM

Moisture, %	19.6
Ash, %	6.1
Volatile matter, %	30.5
Fixed carbon, %	43.8
B.T.U.'s per lb.	9,610
Fuel ratio	1.35

Specimens taken from the top, middle and bottom of the seam in the Celtic and old Sunshine mines, and, at intervals of 6 in., from the new Sunshine mine, were examined through the microscope.

Microscopically the samples from the Celtic mine indicate a predominance of dense groundmass in which are embedded fragments of woody material, leaf cuticles, fragmentary cell walls, some fusain and a few spores. Resin bodies are present, but are strikingly fewer in number than in No. 1 seam. Fig. 6 illustrates a vertical section of a fusain fragment. Some of the cells have shattered walls that display the typical "bogenstructure" ("structure en étoile" or "structure en arc"), while other cells have thick walls and are less broken. A plant structure is shown in Fig. 16 which may be a spore; this section also illustrates the preponderance of dense groundmass in No. 2 seam in the vicinity of the Celtic mine.

Coal samples from the Sunshine mines, old and new, show a much larger proportion of woody structures. The microscope indicates that the coal in the old mine consists of woody material slightly in excess of dull attritus, the upper portion of the seam being more woody than the lower. The lower part has a silky or waxy lustre owing to the bright and dull varieties being present in about equal proportions. The dull layers contain much macerated, highly decomposed wood, fragmentary cell walls, a few spore-like bodies, small fragments of charred wood, and a few leaf cuticles. Resin is present only in very small quantity. In the new Sunshine mine, woody structures form almost all the coal, which is bright in lustre. Only near the bottom were dull attritus layers more abundant, and, in these layers, several bodies that may be spores were observed.

The old Sunshine mine is about one mile north of the Celtic, and the new Sunshine mine is about one-half a mile still farther north. It would appear as though there were different conditions existing in the peat swamp at the time of plant accumulation, and different types of coal resulted. The abundance of dull material with spores in the Celtic coal indicates that the water cover was probably greater at that place, and less where the old Sunshine mine was situated, whereas the swamp was more heavily forested at the location of the new Sunshine mine. The presence of large pieces of silicified wood in the latter place, and the occurrence of a still greater number of silicified tree trunks in the seam farther north near Rosedale, would tend to support this possibility.

Silicified Tree Trunks of No. 2 Seam

The occurrence of large, hard, siliceous masses cutting through No. 2 seam in the new Sunshine mine has been noted. Associated with the masses, along their border, are zones of structureless, waxy-lustred coal also cutting across the normal bedding planes. One mass in particular had many smaller ones branching off at the base. While visiting the mine, the writer and the mine officials thought that these masses were hard, fine-grained sandstone "veins", filling fissures in the coal. Microscopical examinations, however, proved that these masses are tree trunks, and the coal zones along the borders represent the bark of the former trees. The microstructure shows the masses to be of a composition similar to that of the smaller tree trunks of No. 1 seam. The

branching masses at the base of the trunks were probably the roots. These plant remains have been determined as belonging to the conifer *Cupressinoxylon*, the same group to which the silicified trees in No. 1 seam belong.

No. 5 Seam

Next to No. 1 seam, No. 5 is the most important in this district. This seam varies in thickness from 3.5 to 5.5 ft., with local lenses of bone and shale. The roof consists of shale and bentonitic sandstone, and the floor of shale. The interval between No. 5 and No. 1 seams varies from 47 ft. in the western part of the area to 35 ft. at the eastern end. Samples were examined from the Monarch (No. 1 is also worked here), Newcastle, Premier, Newcastle Junior, Elgin and Midwest mines.

The most pronounced physical feature of No. 5 seam is the bright glossy lustre of the coal almost throughout its total thickness. Near the base some duller streaks are noticeable. This uniformly bright lustre distinguishes this seam from No. 1, which has a more pronounced laminated appearance. On almost every bedding plane of No. 5 seam there may be noticed a thin film of fusain.

The coal has a tendency to slack on exposure to air, more so than is the case with the coal of No. 1 seam. A typical analysis (11, p. 56) of the coal from No. 5 seam (as mined) is shown in Table V.

TABLE V

COAL FROM NO. 5 SEAM

Moisture, %	19.7
Ash, %	6.7
Volatile matter, %	30.5
Fixed carbon, %	43.1
B.T.U.'s per lb.	9,460
Fuel ratio	1.40

On closer examination of hand specimens of this coal and by studying them through the microscope, it is observed that the seam is not homogeneously woody throughout, as would be expected from its general brilliant lustre. As a rule, there is a fine lamination of bright and silky lustred streaks. Microscopically, the bright streaks exhibit cellular structures in various states of preservation, some with cell walls almost completely flattened, others displaying a net-like arrangement of cells filled by resin or other plant secretions. Fig. 8 illustrates this latter type. Fig. 18 shows a portion of a bright lens, composed of a flattened stem in which the annual rings have been preserved. These rings indicate that the climate was seasonal during the period in which these plants were growing, contrasting with that of most Palaeozoic coal-forming periods when temperatures were subtropical and fairly uniform. The duller streaks of silky or wax-like appearance contain a preponderance of macerated woody fragments. The finely laminated character of the coal is shown in Fig. 17.

Fusain as thin films on the bedding planes and as fragments in the duller zones is common in No. 5 seam. Some extremely delicate structures are visible through the microscope (Fig. 5). Many annual rings, medullary rays, and border pits (Fig. 9) are clearly visible. In the samples from Newcastle Junior mine, it was observed that fusain was not as prevalent as in those from other mines, neither in the dull layers nor as thin films. It would appear

as though the water cover were deeper in this portion of the peat swamp. The nature of the floor in the Newcastle Junior mine favors this possibility. The floor, as shown in the entries that run in a southwesterly direction, has a slight downward grade followed by an upward slope. The coal seam is also thicker at this point. There was probably a local basin here at the time of vegetable accumulation.

A few spores occur, and also several bodies which may be spores, especially near the base of the seam. One type, although not present in abundance, has discontinuous walls and has been found to be more abundant in No. 5 seam than in No. 1. Other structures are common also in the duller laminae. Much corticular tissue is well preserved. Leaf cuticles can be recognized. Resin particles are very numerous, especially near the upper part of the seam, whereas at the base of the coal they are almost lacking. The resin occurs as particles in the duller layers and as cell fillings of the bright lenses. In some of the bright lenses the cell walls have almost completely disappeared, and the resistant resin-filling is all that remains to indicate former cellular structure. Some oval-shaped bodies with irregularly shaped cells that may be seeds(?) or pollen grains (?) are shown in Fig. 19; in the same illustration, among other bodies, there is a portion of a leaf cuticle.

No. 7 Seam

At one time the Brooks mine extracted coal from this horizon. The thickness of the seam varies from less than a foot to a maximum of about six feet. At Brooks mine, 42 in. of coal, with 13 in. of bone near the centre, are exposed. A typical analysis (11, p. 56) of this coal (as mined) is shown in Table VI.

TABLE VI

COAL FROM NO. 7 SEAM

Moisture, %	18.6
Ash, %	8.3
Volatile matter, %	29.8
Fixed carbon, %	43.3
B.T.U.'s per lb.	9,430
Fuel ratio	1.45

Only three samples were available for microscopic examination; from the top, middle, and bottom of the seam at Brooks mine. The samples indicate that the coal is finely laminated at the top, with bright woody coal in excess, and that it grades downwards into dull coal at the bottom.

Microscopically the top sample shows a rather streaky or banded character. The dull parts are composed largely of macerated material, streaks and bands derived from soft woods, leaf cuticles, resin and cell fragments, and a few spores. Fig. 3 illustrates a portion of the top sample, showing the macerated materials and a probable spore (?).

The middle sample contains much dense, structureless attritus, several leaf cuticles and some doubtful spores.

The bottom sample of this seam also is largely dense, dull material, representing the "muck" of the peat stage. Through this dense groundmass run thin bright streaks of soft structured vegetation, probably grasses (?). There are some indistinct spores and leaf cuticle. Fig. 10 illustrates the denseness

of the attritus and some embedded leaf cuticles. A few spore-like bodies, similar to the ones with discontinuous walls found in No. 5 seam, but smaller and fewer in number, were observed in these samples from No. 7 seam.

Correlation of Seams by Aid of the Microscope

The Drumheller coals were studied with one of the main objects being to determine whether the microscope could be employed to correlate the upper Cretaceous coal seams. The stratigraphic relations had already been determined in this field, and, in the microscopic study, an endeavor was made to establish correlating factors that could be applied to other coal occurrences where the stratigraphic relations were not known.

In the Appalachian and other coal fields of Palaeozoic age, seams have been successfully correlated by the size and shape of the spores they contain. The spore content of the Drumheller coals is not large, nor are the spores of different seams much diversified in character. There are a few spores that do appear to be distinctive of one seam only, such as that shown in Fig. 13, which has been found in No. 1 seam only. Although these spores do appear to be characteristic of certain seams, they are so few in number that intensive study of a large number of specimens would be necessary to discover their occurrence. It may be mentioned here, also, that the spores of the other seams and of the other horizons of Alberta coals that were studied are similarly few in number and are lacking in distinctive character. It is concluded that the spore content of the Cretaceous coals of Alberta are not of diagnostic value for correlating seams.

There are some broad, indefinite features that differentiate the various seams in the Drumheller region:

No. 1 seam consists predominantly of woody components throughout, with the exception of the upper few inches that have more attritus. The resin particles are more numerous near the base of the seam. Several oval bodies, probably corticular tissues, with constrictions giving a dumb-bell shape, are more characteristic of No. 1 seam than of the higher seams. The few spores that do occur are more numerous near the roof of the seam.

No. 2 seam has no definite distinctive features, unless the slightly greater number of leaf cuticles is considered.

No. 5 seam is largely of woody origin, but in contrast with No. 1 seam there is slightly more attrital material and a few more spores at the base of the seam. Resin particles are more abundant in the upper portion of the seam; this feature also is in contrast with No. 1, where the resin is more prevalent in the lower part.

No. 7 seam, examined only at one place, appears to be composed largely of the dull type of coal and soft types of vegetation. Leaf cuticles are also abundant in this seam.

These features, although apparent after much study of the Drumheller coals, are too indefinite to be of value for purposes of correlation in other districts. It is possible that botanical classifications of the various plant

remains found in the seams may be of correlating value. The excellent preservation of structures in the fragments of fusain should make such a classification possible. Further experience, however, is necessary in interpreting these structures.

The Ardley or No. 14 Seam

No. 14 seam occurs close to the top of the Edmonton formation (see Table I) and is mined in the Ardley, Big Valley, and Carbon (northern part) coal areas. The seam mined in the Pembina area corresponds in stratigraphic position to the Ardley seam. The thickness of the seam, including partings of mineral matter, is variable, owing principally to variations in the thickness of the partings. The range of analyses of this coal (as mined) from the different localities is indicated in Table VII (11, pp. 47, 53, 55).

TABLE VII

COAL FROM ARDLEY OR NO. 14 SEAM

Moisture, %	17.5–21.8
Ash, %	8.1–13.3
Volatile matter, %	27.0–30.6
Fixed carbon, %	38.6–44.8
B.T.U.'s per lb.	8,370–9,500
Fuel ratio	1.35–1.50

The coal is usually of medium brightness and is blocky in appearance. A noteworthy characteristic of this seam in almost all its known occurrences is the relative abundance of fusain as thin films and small lenses. This feature is especially characteristic of the upper portion of the seam.

Hand specimens from No. 14 seam in Ardley, Big Valley, and Lakeside (Pembina area) have been examined. The microscopical nature of the coal has been studied in samples from the Lakeside collieries where the seam is known as the Pembina or Wabamun seam.

The mineable portion of the seam at Lakeside averages about eight feet in thickness. The upper five feet of coal has a steel-grey lustre and is finely laminated. The lower three feet of coal is more massive and has a bright silky lustre.

The bright lenses of the upper portion of the seam, and the bright bands of the lower, show woody textures both in hand specimens and through the microscope. The bright lenses of the upper part show cellular structures that are almost obliterated by decomposition, and the cell cavities are scarcely visible owing to flattening of the cell walls. Resin particles are few in number in this upper region. The bright zone at the base of the seam, however, shows a better state of preservation and it probably was originally a hardier type of vegetation. Resin is more abundant and much of it occurs as cell fillings in the lower part of the seam. Resin particles occurring as remnants of former cellular structure are shown in Fig. 12.

The duller streaks, common in the upper part of the seam, are composed of attrital material—fragments of cell walls, macerated wood, a few pollen grains (?), leaf cuticles, and a considerable number of fragments that have been converted to fusain—embedded in a proportionately large amount of dense groundmass. Few spores were recognized. The fragments of fusain

are noteworthy for the abundance of their number and for the delicate nature of plant structures that have been preserved. There are many small lentilles of mineral matter in the upper part of the seam, and fusain appears to be more abundant when associated with this mineral matter (cf. p. 280). The occurrence of this fusain in relatively large quantity probably influences the quality of the coal and offers a partial explanation of the high carbon ratios that characterize the Ardley seam wherever it is mined. In the foothills near the Rocky mountains, there are some coals that, besides being of older age, have been subjected to much greater pressures and are of higher rank than the coal of the Ardley-Pembina seam. Yet, the carbon ratios of this seam are the higher, showing, as pointed out by the writer in another paper (5), that the carbon ratios in this region are not an index of the amount of pressure and metamorphism to which a coal and its enclosing rocks have been subjected.

Lower Cretaceous Coal at Brule

General Features

The Brule coal field is situated on the Canadian National Railway 185 miles west of Edmonton, and is partly in the foothills and partly within the Rocky Mountains. At Brule mines, the strata of the Kootenay formation, in which the coal occurs, are twisted into a complicated series of folds and faults, and they are overridden by the Palaeozoic limestones that form the front range of the mountains. Several coal seams, ranging in thickness from less than a foot to more than 10 ft., occur in this region. Locally some of the seams are thickened and thinned owing to squeezing by intense mountain-building pressures. The complicated structures make the ascertaining of the stratigraphic relations of the seams a difficult task. In the mine workings the relations existing among five seams may be observed, and Table VIII is a section given in descending order, as exposed in the main slope.

TABLE VIII

Section at Brule mine in descending order

Coal—No. 1 seam	4 to 5 ft.
Sandstone	360 ft.
Coal—No. 2 seam	5 ft.
Sandstone	220 ft.
Coal—No. 3 seam	9 ft.
Sandstone	62 ft.
Coal—No. 4 seam	4 ft.
Sandstone	72 ft.
Coal—No. 5 seam	1 ft.

Coal has been extracted from only two of these seams, namely, Nos. 2 and 3.

There is a marked difference in the physical characters of these two seams, the coal of No. 3 seam being crushed into a fine, flaky condition, whereas No. 2 seam is compact, with blocky coal. Apparently No. 3 seam and the adjacent strata bore the brunt of the intense mountain-building pressures, and acted as a cushion protecting the strata adjacent to No. 2 seam. The laminated nature of the coal of No. 3 seam is not apparent in hand specimens, owing to the presence of polished, slickensided, fracture planes produced by extreme pressures. Lump samples of this coal are difficult to obtain, the slightest force being sufficient to break the specimens into small fragments.

No. 2 seam, on the other hand, is relatively hard and compact, and the lamination of dull and bright coal is clearly apparent. The analyses of these coals (as mined) give the values shown in Table IX (7, pp. 52-53).

TABLE IX

COAL FROM BRULE

	No. 3 seam	No. 2 seam
Moisture, %	1.4	1.2
Ash, %	18.8	13.2
Volatile matter, %	18.2	21.1
Fixed carbon, %	61.6	64.5
B.T.U.'s per lb.	12,300	13,330
Fuel ratio	3.40	3.05
Coking property	Poor	Good

The high ash values in the analysis of No. 3 seam is caused by the crushed nature of the coal and hanging wall permitting the inclusion of mineral matter in the coal from the adjacent rocks.

MICROSTRUCTURE OF BRULE COALS

No. 3 Seam

Very little information can be obtained regarding the constitution of the coal in No. 3 seam from a study of hand specimens, owing to the slickensided nature of the surfaces. Microscopic methods are necessary to obtain such information. Several specimens from various portions of this seam were polished and etched. Most of the coal was found to consist of numerous small, bright lenses of woody origin embedded in a relatively abundant, dull groundmass of attrital material. The bright lenses show, through the microscope, compressed cellular structures with partly decomposed walls. The duller bands are composed chiefly of densely packed, macerated wood and fragments of cell walls. Several fragments of fusain and particles of resin occur also in the duller zones. No spores were observed in the specimens examined. Fig. 20 illustrates the microscopical nature typical of No. 3 seam; lenses of bright woody coal may be seen in contact with attrital material containing particles of resin and plant debris, some of which has been converted to fusain. Near the base of the seam the coal consists largely of highly decomposed and compressed material of woody origin.

No. 2 Seam

No. 2 seam, stratigraphically 220 ft. higher than No. 3, may be considered in three parts. The upper two feet of coal is of medium lustre with fine, bright and dull laminations. Below this coal is a band, averaging about two feet in thickness, of massive, hard, grey coal in which lamination is indistinct. At the base of the seam the coal is banded with bright lenses predominating.

Microscopically the upper portion of the seam consists of closely packed wood tissues. The cell walls are compressed, indicative of the great stresses to which the coal has been subjected. A few grains of resin and numerous fragments of wood structures occur in the duller streaks. The resin content of this portion of the seam is strikingly smaller than that of the lower zones.

The grey coal, although exhibiting a uniform appearance in hand specimens, shows some structure on a polished surface. Numerous small, round and

oval objects may be observed. On etching with chromic acid most of these small bodies are acted upon and small holes, each the size of a pin hole, are left on the surface. Through the microscope the coal is found to consist principally of highly decomposed woody material with the fibres streaming around the small round objects. These objects were determined as being resin particles, mostly spherical in shape with a diameter of about 0.3 mm. A few of the particles have an oval shape, ranging up to 1 mm. in length and 0.25 mm. in width. Some of the resinous bodies are more resistant than others to the action of chromic acid, and are unaltered by that reagent.

Some thin streaks of dull coal occur in the mass of grey coal. These duller zones consist of macerated woody materials, resin, and a few fragments of fusain. One microspore was observed in this coal. Fig. 21 shows a fragment of fusain. The fibres are seen to curve around the black cavity in which resin was present previous to etching. In the charred fragment some cells are thick walled and relatively unbroken, whereas the thin-walled layers have been crushed, producing typical "bogenstructure".

The grey lustre of this coal is caused chiefly by the extraordinary abundance of resin, and partly by the state of the material in which the resin is embedded. The wood fibres have been almost completely decomposed, and have almost reached a "gelified" condition. The appearance of this coal is very similar to that of the grey coal of No. 1 seam in the Drumheller area that has previously been described (see page 286). The cause of the grey lustre, however, is not wholly the same for both occurrences. In the Brule coal the lustre results mainly from the large number of resin particles, while at Drumheller it is the result of innumerable conchoidal surfaces caused by the rapid drying of coal in a gel-like condition. It is interesting to note, however, that a partial gel-like condition appears to have been present also in the grey coal at Brule, and also that this coal is lower in moisture than the average coal of the seam. Frequently there occurs a thin band of soft, soap-like shale separating the grey coal from the upper portion of the seam. This feature is somewhat analogous to the occurrence of bentonite with the Drumheller grey coal.

It would be expected that the high resin in the Brule coal would have a noticeable effect on the quality of the coal. It is found that such is the case—the grey coal is higher in volatile matter and possesses better coking properties than the average coal of No. 2 seam. An analysis of the grey coal (as mined) gives the values shown in Table X (7, p. 53).

TABLE X

GREY COAL FROM BRULE

Moisture, %	0.9
Ash, %	9.6
Volatile matter, %	26.3
Fixed carbon, %	63.2
B.T.U.'s per lb.	13,820
Fuel ratio	2.40
Coking property	Good

The zone of laminated coal below the grey coal and at the base of No. 2 seam consists of streaks and small lenses of bright material in a more abundant duller type of coal. The bright lenses show a microstructure of greatly compressed wood cells. The duller zones are composed chiefly of macerated wood

and a large quantity of crushed cell fragments. Resin particles are more abundant than they are in the top bench of No. 2 seam, but they are much less numerous than those in the grey coal. Fusain is not abundant, and no spores were observed in this coal.

Acknowledgments

Financial assistance during this study of Alberta coals was given for four years by the University of Toronto and, for one year, by the National Research Council of Canada. The Geological Survey of Canada, by employing the writer to work in various areas of Alberta, gave him an opportunity to study conditions in the field and to collect specimens both during and after the working season. The research was sponsored in many ways by Dr. E. S. Moore, Department of Geology in the University of Toronto. To Prof. A. MacLean, of the same department, acknowledgment is also due for the interest he took in this work. Prof. J. E. Thomson kindly permitted the use of polishing machines and a metallographic camera. Gratitude is expressed to Prof. R. B. Thomson for his interest and assistance in the botanical phase of the problem. The writer is deeply grateful to Dr. J. A. Allan, Professor of Geology, University of Alberta, for his kind advice and for the many coal samples supplied by him. The author wishes to express his grateful appreciation to the officials at several mines for their courteous reception and assistance when he visited and collected samples from their mines.

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All sections, except those in Figs. 13 and 14, are of polished and etched surfaces.

Plate I

Fig. 2. *Vertical section (× 60) from Rosedeer mine, No. 1 seam, Drumheller. The contact of dull and bright coal is shown, the bright band forming the lower half of the illustration is almost completely decomposed, but the flattened cells are evident. The duller part above contains lenticles of decomposed woody material.*

Fig. 3. *Vertical section (× 60) from Brooks mine, No. 7 seam, Drumheller; top of seam. A medium-lustred coal composed largely of macerated, decomposed wood is shown. The oval body at the left centre is of uncertain origin.*

Fig. 4. *Vertical section (× 60) from Rosedeer mine, No. 1 seam, Drumheller; 3.5 ft. below top of seam. Some well preserved fibro-vascular bundles (upper right), corticular structures (centre) and other fragmentary objects are shown embedded in a dull groundmass.*

Fig. 5. *Vertical section (× 120) from Monarch mine, No. 5 seam, Drumheller; 4.5 ft. below top of seam. Some delicate cells are well preserved in this fragment of wood which has been partly converted to fusain.*

Fig. 6. *Vertical section (× 60) from Celtic mine, No. 2 seam, Drumheller; middle of seam. Charred wood (fusain) is shown with well preserved, thick walled cells and thinner broken cell walls.*

Fig. 7. *Vertical section (× 60) from Rosedeer mine, No. 1 seam, Drumheller; near base of seam. Laminated bright and dull layers are shown. The bright woody parts have highly compressed cells.*

Fig. 8. *Vertical section (× 60) from Premier mine, No. 5 seam, Drumheller. Bright coal, showing woody, cellular structure.*

Plate II

Fig. 9. *Vertical section (× 360) from Elgin mine, No. 5 seam, Drumheller; 6 in. below top of seam. Some fusain, highly magnified, is shown. The cell walls have small cavities, or border pits.*

Fig. 10. *Vertical section (× 60) from Brooks mine, No. 7 seam, Drumheller; bottom of seam. A typical dull coal is shown with thin streaks of cuticle embedded in a dense matrix.*

Fig. 11. *Vertical section (× 60) from Monarch mine, No. 1 seam, Drumheller; near top of seam. The long flattened body above the centre is similar to ones found in Japanese and Australian coals (see text, p. 284). Small particles of resin and fragmentary materials are also shown embedded in dark groundmass.*

Fig. 12. *Vertical section (× 60) from Lakeside mine, Pembina area; 7 ft. below top of seam. This section is composed almost entirely of small particles of resin. The linear arrangement of the particles indicates that they were fillings of former cell cavities, the walls of which have been decomposed.*

Fig. 13. *Thin section (× 60) vertical to bedding, from Western Commercial mine, No. 1 seam, Drumheller; near base of seam. A well defined spore is shown a short distance below the centre. The white irregular patch at the right represents a hole in the thin section.*

Fig. 14. *Thin section (× 60) of silicified wood, Rosedeer mine, No. 1 seam, Drumheller.*

Fig. 15. *Vertical section (× 60) from Rosedale mine, No. 1 seam, Drumheller; 3 ft. below top of seam. A group of corticular tissues in dull coal. Narrow band of highly decomposed anthraxylon.*

PLATE III

FIG. 16. *Vertical section (× 120) from Celtic mine, No. 2 seam, Drumheller. The prominent structure has not been determined. It may be a spore (?). The remainder of the section is composed chiefly of dense groundmass with a small quantity of attritus.*

FIG. 17. *Vertical section (× 60) from Elgin mine, No. 5 seam, Drumheller; middle of seam. Streaks and bands of woody material are seen occurring in dull coal containing fragmentary structures. The oval structure at the right is probably a resinous body, and the one at the left, below the middle, is another type of resinous body.*

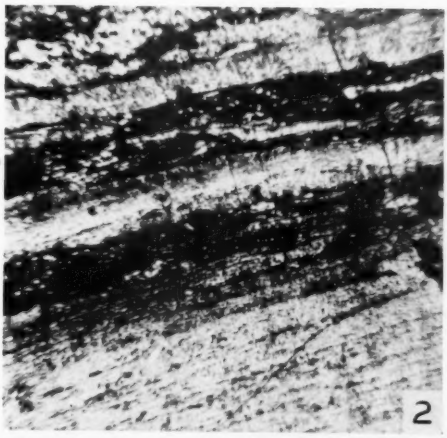
FIG. 18. *Vertical section (× 60) from Elgin mine, No. 5 seam, Drumheller; 3 ft. below top of seam. A portion of a bright lens composed of a flattened stem is shown. The annular rings are clearly shown.*

FIG. 19. *Vertical section (× 120) from Elgin mine, No. 5 seam, Drumheller; middle of seam. Oval bodies, such as that at right centre, may be seeds (?) or pollen grains (?). In lower left corner is a portion of a leaf cuticle.*

FIG. 20. *Vertical section (× 60) from Brule mine, Kootenay formation, Brule area; top of No. 3 seam. Bright and dull coal and fusain are illustrated. In the upper part of the section, the flattened nature of the cells is shown in the band of bright coal. Relatively large particles of resin are shown near the centre.*

FIG. 21. *Vertical section (× 120) from Brule mine, grey coal of No. 2 seam. Wood partly converted to fusain is shown, curving around the large, dark cavity which represents the former position of a fragment of resin that had been removed by etching.*

PLATE I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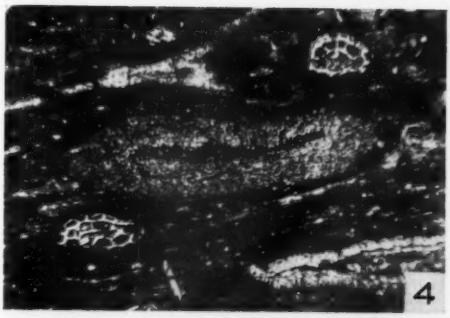
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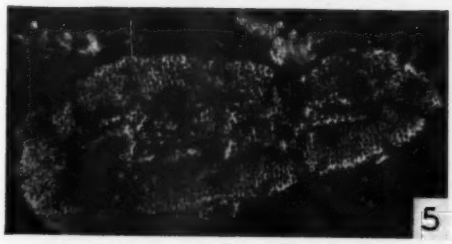
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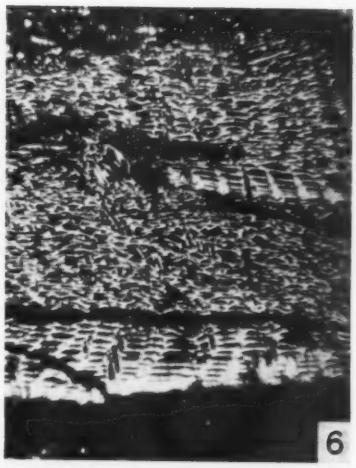
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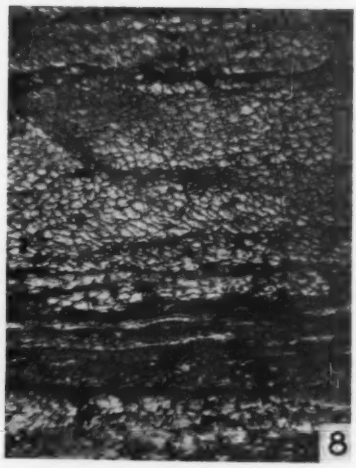
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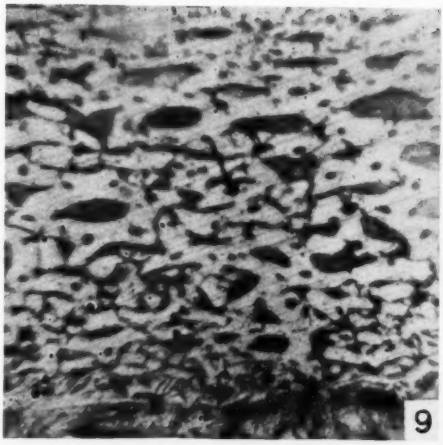
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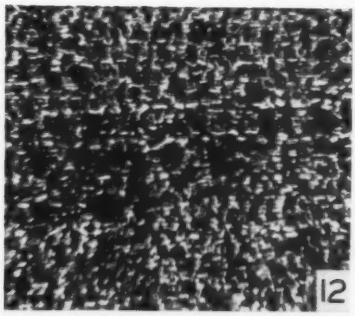
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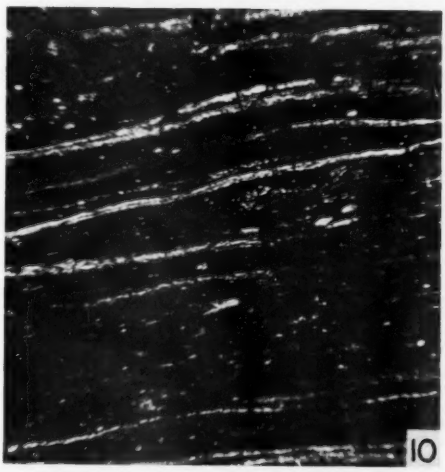
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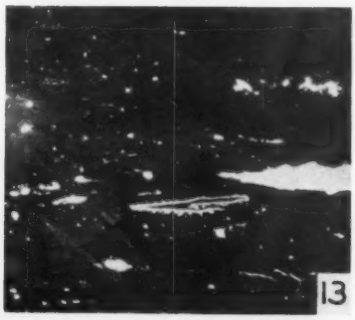
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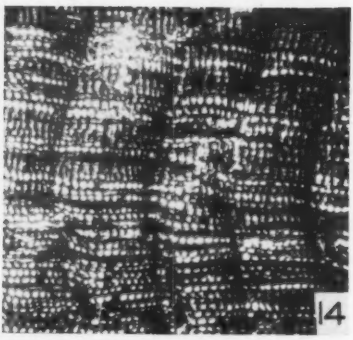
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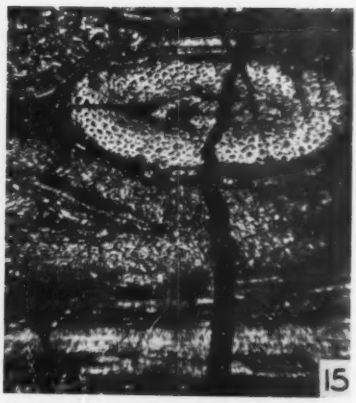
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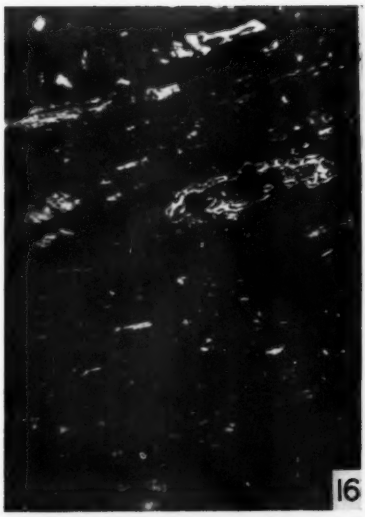
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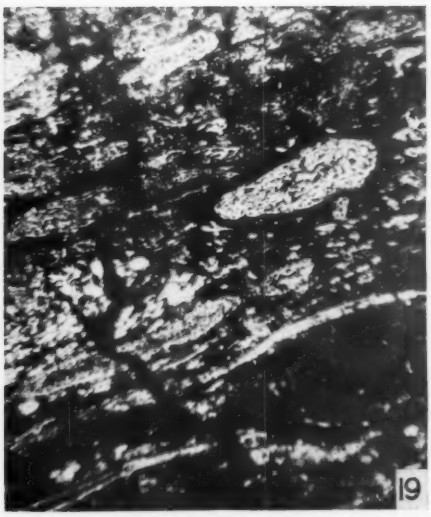
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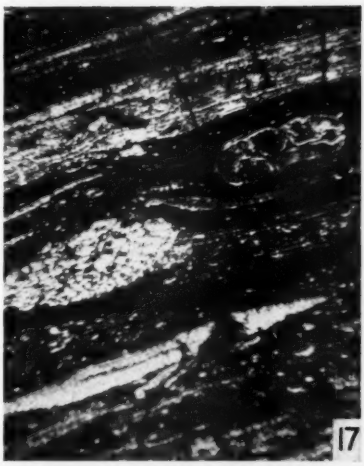
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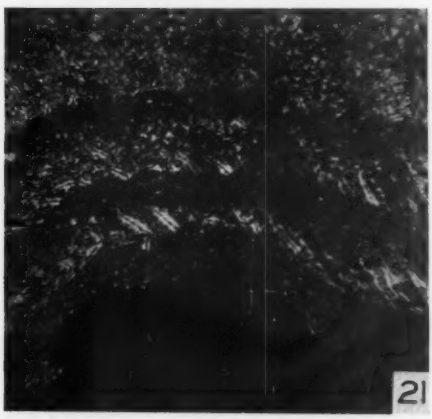
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A METHOD FOR ACCURATE TITRATIONS[1]

By D. B. Pall[2]

Abstract

A method that renders titrations having indistinct color end points more accurate, and that makes possible their use with colored solutions has been developed. Application of the method to the problems of the sugar refinery gave satisfactory results.

Introduction

This method was developed in the laboratories of the St. Lawrence Sugar Refineries to meet particular needs, but it is of general application.

The writer's experimental work was carried out with solutions that were to be titrated for acidity or alkalinity, and that ranged in pH between 6.0 and 8.0. A pH of 7 is taken as the end point in these titrations. Many of these solutions contain a considerable quantity of weak organic acids and bases, and are therefore more or less strongly buffered. For this reason, the indicator used, in contrast with that employed in the case of a strong acid-strong base titration, undergoes no sharp color change at the end point. Moreover, since the solutions are usually colored, titration to a definite color as an end point is also unreliable. Some of the solutions are so dark that the presence of the indicator is completely obscured, unless the dilution is excessive.

Apparatus

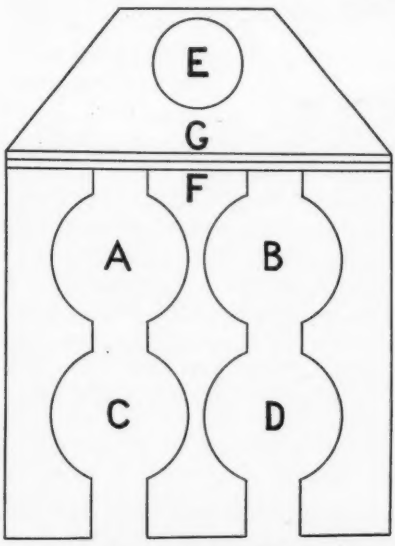

FIG. 1. *Plan of the apparatus.*

A plan of the apparatus devised to meet these difficulties is illustrated in Fig. 1. *A*, *B*, *C* and *D* are arranged to receive test tubes about 3 cm. in diameter and 20 cm. long, and having a capacity of 130 cc. In *B* is inserted a glass sealed, sterilized tube containing a standard solution. This standard is essentially a clear solution at the end point of the titration. The author used as a standard a solution buffered at pH 7, containing an amount of the indicator (Bromthymol Blue) sufficient to give a reasonable depth of color when viewed transversely. In *A* is an identical sealed tube containing water only. *C* and *D* receive open tubes of the same dimensions. To tube *C* is added the solution to be titrated, plus a proportion of indi-

[1] *Manuscript received July 17, 1936.*
Contribution from the laboratory of the St. Lawrence Sugar Refineries, Montreal, Canada.
[2] *Chemist, St. Lawrence Sugar Refineries, Limited, Montreal.*

cator similar to that in the tube *B*. *D* is also filled with the solution, but no indicator is added. *C* and *D* are fitted with vertical stirrers.

F is a frosted glass plate. Behind it is placed a sheet of glass, *G*, which is of the same color as the standard in tube *B*. Its purpose is to filter out all other colors of light, so that the color due to the indicator will predominate over that of the solution itself when viewed from the front. *E* is the source of light, whose nature will also be determined by the color of *B*. In the writer's experiments, in which Bromthymol Blue was used as indicator, a daylight lamp was found suitable. The lamp is fitted with a reflector as shown.

Use of the Apparatus

Through *B* and *D* are seen superimposed the colors of the solution and of the standard. When the solution in *C* is at the end point of the titration, it will also contain the colors of the solution and of the standard, in a single tube, while *A* compensates for the extra tube and thickness of liquid on the other side. Under these conditions, therefore, the colors seen on looking through either side towards *F* are identical. Hence the procedure in using the apparatus is simply to titrate the solution in *C* until the colors on the *A*-*C* and *B*-*D* sides match.

Obviously, transmitted light only may be allowed. For this reason, the apparatus is either set up in a poorly lighted part of the room or provided with a shield through which *C* and *D* may be seen. Such a shield is easily constructed by removing the ends from a rectangular closed box, which is then fitted in front of the apparatus.

Preparation of Standards

The preparation of a permanent standard may present some difficulty. In the case of acidimetric-alkimetric titrations, in which pH 7 may be taken as the end point, Bromthymol Blue is suitable as an indicator. A buffered solution is prepared by titrating a normal ammonium acetate solution with 0.05 *N* acid or base to pH 7, as measured by a potentiometer and quinhydrone electrode. To 100 cc. of this solution a suitable quantity of the indicator is added. The end of one of the large test tubes is drawn down to a narrow neck, and the standard added: the tube is then sealed by drawing off at the constriction. It was found necessary to sterilize these standards. For this purpose a 20 min. treatment at 120° C. in a steam chest was found satisfactory, and did not alter the color.

The method is of course not limited to acidimetric determinations, and may be applied wherever a color is used to distinguish an end point. The presence of suspended matter is not a disadvantage as long as the solution is translucent.

STUDIES IN THE SYSTEM CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

IV. VAPOR PRESSURE STUDIES IN THE PRESENCE OF CELLULOSE AND WOOD[1]

By P. E. Gishler[2] and O. Maass[3]

Abstract

A new technique has been developed for the purpose of studying, by means of vapor pressure changes, the effect of wood and cellulose on the system calcium-oxide–sulphur-dioxide–water. Preliminary experiments are described. A sample calculation has been made, to indicate that vapor pressure changes might be used to determine the relative rate of consumption of sulphur dioxide and calcium oxide during the cooking of wood. Cellulose does not yield carbon dioxide in appreciable quantities during cooking.

Introduction

It was believed that a careful study of the vapor pressures of the system calcium-oxide–sulphur-dioxide–water in the presence of wood might serve as a means of elucidating the mechanism of sulphite cooking. This work serves two purposes. (i) It completes a study of the system calcium-oxide–sulphur-dioxide–water in which equilibria have been determined. (ii) It introduces a new method of studying sulphite cooking. The two are closely related however as in the latter case one more component, *i.e.*, wood, has been added to the system. In the time available it was impossible to do a large number of experiments. The chief object of the work was to develop a technique for the study of this system. Aside from this, several matters of interest have been observed.

Further information regarding the mechanism of sulphite cooking was sought through the measurement of the vapor pressures of the system during cooking. Two essential conditions to make this possible are (i) the experimental technique, whereby accurate determinations of vapor pressures could be made under perfectly controlled conditions of temperature and liquor composition, and (ii) a knowledge of vapor pressures of sulphite liquor of known composition and at a known temperature. Both of these conditions have been attained in the course of a study of the system calcium-oxide–sulphur-dioxide–water.

A number of cooks were therefore carried out in which pure reagents of accurately known concentrations were used. Both spruce woodmeal and pure cellulose were cooked, the time of cooking varying from 8 to 30 hr. Vapor pressures were carefully determined throughout each experiment. The temperature was 130° C.

[1] *Manuscript received June 12, 1936.*
Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada.

[2] *Holder of a bursary and studentship under the National Research Council of Canada.*
[3] *MacDonald Professor of Physical Chemistry, McGill University.*

Apparatus

Four bulbs placed in series with a high pressure sulphur dioxide cylinder were used to redistill the sulphur dioxide several times in order to purify it. These were connected to a larger bulb of carefully determined volume and a two armed manometer, which served to measure pressures of the gas before and after introduction to the filler tube.

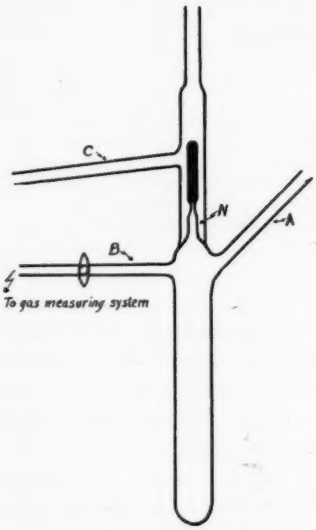

FIG. 1. *Filler tube.*

The filler tube, the reaction cell and the manometer system are shown in Fig. 2. It was necessary to make up the solutions separately before adding them to the wood-meal. The filler tube, Fig. 1, contained a triple seal with an inner small nipple, which could be broken by dropping an iron core on it. The core was sealed into a side-arm and could be manipulated by means of an external electromagnet.

The cell, *F*, was made of 1 in. Pyrex tubing and built to withstand 100 lb. pressure. It was immersed in a bath of dibutyl phthalate, which contained the necessary stirrers, *E*, and heaters, *H*. The bath could be heated to 130° C. in 45 min. and regulated to within 0.1° C. The cell was connected to a large constant-level, closed-end manometer, *M*, capable of measuring pressures as high as 100 lb. per sq. in. with an accuracy of 0.3%.

The bent tube, *S*, served as a frozen mercury seal during an experiment. *S* was connected to the evacuating apparatus. The stem of the reaction cell was connected to the manometer, *M*, by means of the lagged tubing, *L*. This tubing was wound with resistance wire.

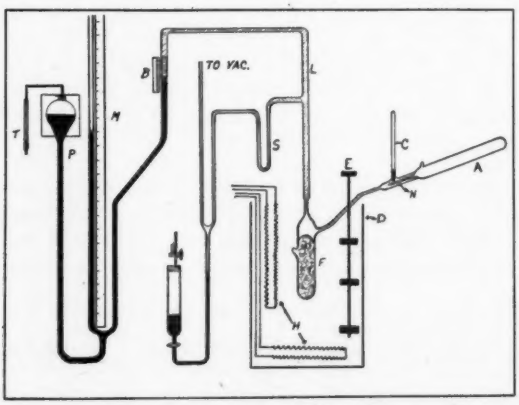

FIG. 2. *Reaction cell, temperature control and manometer system.*

Procedure

Pure calcium oxide was prepared by grinding Iceland spar to a fine powder and subjecting it to a temperature of 1000° C. for a week in the presence of a current of air, free from carbon dioxide and water vapor.

Side-arm *B* of the filler tube (Fig. 1) was connected to the gas measuring system by means of glass tubing of known volume. Evacuation could also be effected through *B*. Side-arm *A* served for the introduction of calcium oxide and water.

A was sealed shut and the filler tube evacuated, after which it was filled with dry air, free from carbon dioxide. *A* was broken open and weighed amounts of calcium oxide and water were introduced. *A* was then sealed off. The next step was to remove the air above the water, together with any dissolved gases. This air could be removed by opening stopcock *B* (Fig. 1) and evacuating the tube. However, a method had to be used whereby a minimum of water vapor was lost. That part of the side-arm *B* to the left of the stopcock was evacuated, and the stopcock was quickly opened and closed. As the pressure of the air above the water was reduced, the dissolved gases came out of the solution. Several such sudden evacuations, conveniently spaced, served to remove all gases from the filler tube.

The desired amount of sulphur dioxide was measured and allowed to pass directly from the measuring bulbs into the filler tube, where it went slowly into solution. Solution was hastened by surrounding the filler tube with ice. The rate at which the sulphur dioxide dissolved could be followed on the manometer attached to the measuring system. When the desired amount had gone into solution, side-arm *B* was sealed off close to the filler tube. The calcium oxide that had caked at the bottom of the tube was dissolved by shaking.

The filler tube was then sealed to the upper side-arm of the reaction cell, *F*, with the nipple facing down towards the reaction cell, as shown in Fig. 2. Side-arm *C* contained an iron core.

The reaction cell was filled with a weighed amount of woodmeal through its lower side-arm, which was then sealed off. The cell contained a perforated glass cap placed about two inches from the top of the cell. This served to prevent the woodmeal from entering the lagged tube leading to the large manometer. The reaction cell was then immersed in the bath.

The bath was heated to 70° C. and the cell evacuated for four hours. Mercury was run into the seal, *S*, which was then surrounded with a freezing mixture of carbon dioxide in acetone. The iron core in *C* was raised with an electromagnet and allowed to fall on the end of the nipple, *N*. This broke the nipple and allowed the sulphite liquor in *A* to drain into the cell. The filler tube was then sealed off near the cell, and the cell kept at 25° C. overnight in order that the wood and the sulphite liquor would reach equilibrium. The lagged tubing was kept at a temperature above that of the bath, to prevent condensation of water vapor. The mercury bulb, *P*, could be raised and lowered in order to keep the mercury level at zero on scale *B*. Pressure

tubing, T, containing a bicycle valve and stem, was connected by means of $\frac{1}{4}$ in. copper tubing to the mercury bulb. Air could be pumped above the mercury, thus making it possible to measure pressures greater than 500 cm. with a mercury column 9 ft. high.

Vapor pressure determinations were made at 25° C. The bath was then heated to 130° C. in 45 min. Vapor pressure determinations were made every half-hour throughout the experiment. A detailed description of the method of determining vapor pressures has been given in a previous paper (2).

Spruce woodmeal was used. Resinous material was removed by washing it with an alcohol-benzene mixture. In one experiment the influence of cellulose (absorbent hospital cotton) was studied. The cotton was purified by refluxing it for 12 hr. at 100° C. with 1% sodium hydroxide solution. It was then washed free of alkali and again refluxed for 12 hr. This procedure was repeated seven times, after which the cotton was washed and acidified with 1% acetic acid. It was washed free of acid and dried at 100 °C. for two days and then stored in an open bottle. A moisture determination made before the experiment was performed showed that the cotton contained 5% of moisture.

Results

One check run was made with no wood present in order to determine what kind of agreement could be obtained with the data secured previously. In one run pure cellulose was cooked. After the material had been cooked for 10 hr. the cell was cooled to room temperature, and the pressure determined. In Run 6 the wood was cooked for 13 hr., after which it was cooled to room temperature and the pressure determined. The cook was then continued for 17 hr. The other three samples were cooked for periods ranging from 8 to 13 hr. The results are shown in Tables I and II.

Discussion of Results

In Experiment 4 no wood was present. The object was to ascertain the influence of wood on the system being studied, and also to determine how long it took for the solution to reach equilibrium. It was found that after two hours the vapor pressure reached a constant value. This was a measure of the time required to reach equilibrium. In Experiment 3, pure cellulose was included and equilibrium was not reached until the fourth hour. This was due to the fact that the liquor could not be stirred, the presence of solid still further slowing down the attainment of equilibrium.

In the experiments with wood, the vapor pressure obtained at 25° C. before an experimental cook was started was slightly lower than that calculated from the vapor pressure data on the system calcium-oxide–sulphur-dioxide–water (2). This is believed to be due to adsorption of some of the excess sulphur dioxide on the surface of the wood and cellulose.

It can be noted from the vapor pressure curves (Fig. 3) that, after a temperature of 130° C. was reached, the vapor pressure continued to rise slowly and regularly for 8 to 10 hr. to a maximum. The pressure then began to fall regularly. Several factors influence the slope of the first part of this curve.

TABLE I

VARIATION OF VAPOR PRESSURE WITH TIME IN THE SYSTEMS INVESTIGATED (TEMP., 130° C.)

Experiment No.	1	2	3	3A
Initial press. at 25° C., cm.	26.5	30.2	28.1	31.5
Time, hr.	Vapor pressure, cm.			
0	412.1	347.8	395.1	401.4
0.5	412.8	349.9		
1.0	414.2		406.1	402.6
1.5	418.4	352.5	407.7	
2.0	419.1	354.8	411.1	409.6
2.5	422.1	357.5		
3.0	424.3	359.4	415.1	412.2
3.5	427.4	362.1		
4.0	429.8		419.0	416.0
4.5	432.5	365.8	419.0	
5.0	435.6	369.0		417.6
5.5	440.2	371.3		
6.0	444.1		419.2	
6.5	446.5	375.2		
7.0	451.1	378.2	420.2	
7.5	455.0	379.0	420.2	
8.0	456.9		420.2	
9.0		386.0	420.2	
10.0		390.0		
11.0		392.5		
12.0		386.9		
13.0		383.1		
14.0				
Final press. at 25° C.	48.5	63.1	31.5	33.4

TABLE II

VARIATION OF VAPOR PRESSURE WITH TIME IN THE SYSTEMS INVESTIGATED (TEMP., 130° C.)

Experiment No.	4	5	6	6A
Initial press. at 25° C., cm.	25.9	24.3	31.5	61.0
Time, hr.	Vapor pressure, cm.			
0	389.6	370.9	337.9	409.0
0.5	416.4		438.2	423.6
1.0	417.7	378.1	440.4	426.7
1.5	423.4	383.0	445.1	428.9
2.0	422.9	386.1	447.6	429.3
2.5	422.2		450.2	430.5
3.0	423.2	395.0	455.3	431.8
4.0		402.2	460.8	435.4
5.5		413.5	471.4	438.9
7.0		420.0	480.6	444.2
8.0		426.7	487.0	449.6
9.0		427.2	479.9	455.4
10.5			466.4	463.1
11.5			461.9	
12.5			458.0	476.5
13.5			454.8	480.8
14.5				491.2
15.5				497.8
16.5				502.0
Final press. at 25° C.		66.6	61.0	134.3

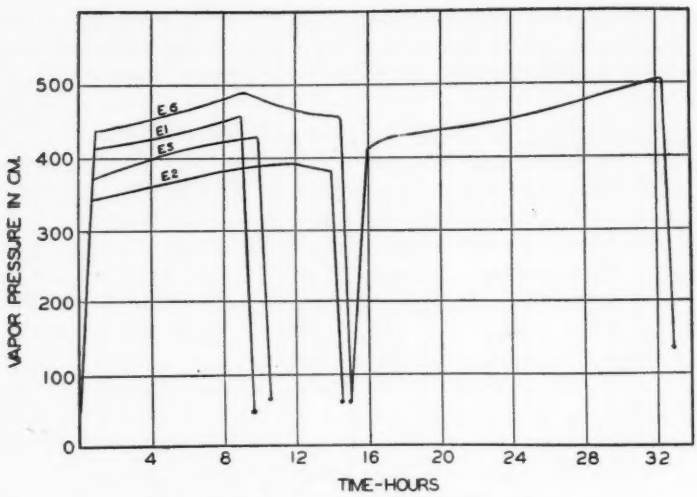

FIG. 3. *Vapor pressure changes during cooking.*

TABLE III

COMPOSITION OF SYSTEMS FOR WHICH THE VAPOR PRESSURE-TIME RELATIONS WERE INVESTIGATED

Experiment No.	1	2	3	4	5	6
Wt. H_2O, gm.	60.96	41.99	44.00	47.34	47.59	48.20
Wt. CaO, gm.	0.804	0.535	0.605	0.598	0.600	0.598
Wt. SO_2, gm.	3.395	2.082	2.486	2.530	2.266	2.627
Wt. wood, gm.	7.23	8.26	3.26*	None	7.94	6.94
Wt. SO_2 (sol.), gm.	3.266	1.873	2.36	2.285	2.074	2.500

* *Pure cellulose used instead of wood.*

If first the liquid and vapor phases only be considered, with rise in temperature the sulphur dioxide in solution tends to enter the vapor phase. This will result in a continued rise in pressure until equilibrium is reached. Another factor influencing the pressure increase is the production of carbon dioxide during cooking. This will be discussed later.

A third factor governing the slope of this curve is the change in concentration of calcium oxide and sulphur dioxide, and, more especially, the relative rate of consumption of calcium oxide and sulphur dioxide during the delignification of wood. Considerable work has been done on this phase of the subject by the use of analytical methods. However, it is believed that changes in the vapor pressure of this system during cooking can be used as a convenient means of following the rates of consumption of calcium oxide and sulphur dioxide. Vapor pressure data for the system calcium-oxide–sulphur-dioxide–water (2) are complete over the temperature and concentration ranges studied in these

experiments. Therefore a comparison of these pressures with values obtained under carefully controlled cooking conditions should yield valuable information on the rate of consumption of calcium oxide and sulphur dioxide. Vapor pressure increases are not necessarily entirely due to a decrease in calcium oxide concentration, for other gases may be formed during cooking.

Considerable work has been done on the quantitative determination of gases that are produced in the delignification of wood. Krüger (4) found that in commercial cooks of birch, the relief gas consisted only of nitrogen, carbon dioxide and sulphur dioxide. The nitrogen was said to correspond to the amount of air left in the digester after filling it with liquor and chips. In the present work care was taken to remove all air. Nepenin and Khviyuzov (6) also found carbon dioxide to be the only gas produced during cooking. They found that the carbon dioxide amounted to 1.43% of the decomposed part of the wood. The small amounts of organic vapors formed may tend to raise the vapor pressure a small amount at elevated temperatures. A quantitative study of the amounts of organic vapors produced during cooking has been made by Partansky and Benson (7). Their results indicate that, in the present preliminary investigation, the influence of these vapors can be neglected without introducing a large error in the calculated results.

The data submitted in this paper are not complete enough to warrant the drawing of definite conclusions. However, the following calculations are included to indicate the possibilities of this method of study. In mill practice the limiting sulphur consumption is approximately 10% of the bone-dry weight of pulp. Bergson (1) claims a yield of 55% pulp in cooks that required only 140 lb. of sulphur per ton of pulp formed. This is an unusually low value. The value used in the following calculations were determined by assuming that fully sulphonated lignin contains 8% of sulphur and that the wood used contained 30% of lignin. The value for the weight of sulphur dioxide consumed, which is 4.8% of the weight of dry wood, appears reasonably accurate.

Opinions differ as to the relative rate of removal of calcium oxide and sulphur dioxide. Recent studies by Mitchell and Yorston (5) and by King, Brauns and Hibbert (3) show that two atoms of sulphur are consumed for every atom of calcium. The results of the following calculations are in agreement with this value.

The results of Experiment 5 are used because a maximum does not appear in the curve, and hence it may be concluded that the wood was not overcooked. In this experiment the sulphite liquor contained 0.6004 gm. of calcium oxide, 2.074 gm. of sulphur dioxide and 7.90 gm. of dry wood. If the consumption ratio of 2 SO_2 per unit CaO first be considered, the required amounts of calcium oxide and sulphur dioxide are 0.166 gm. and 0.38 gm. respectively. If these values are subtracted from the initial calcium oxide and sulphur dioxide contents, the apparent resultant pressure of the system due to the new concentrations can be determined from previous data (2). The pressure was determined as 360 cm. at 130° C. The measured vapor pressure at this temperature in the presence of cooked wood was found to be 427 cm. The excess pressure

of 67 cm. was assumed to be due to carbon dioxide. Any errors introduced at this point would be due to the partial pressure of volatile by-products, but their influence was considered sufficiently low to be ignored. If the ratio of consumption of calcium oxide to that of sulphur dioxide is 2 to 1, then the carbon dioxide value obtained should check with that calculated independently at room temperature after the cook was completed. This could be determined by means of the gas laws, since volume changes of the closed system were known for the temperature changes observed. At room temperature it was found that the excess pressure due to carbon dioxide amounted to 48 cm. This becomes 68 cm. when calculated to 130° C., which is in very close agreement with the independent determination at 130° C., *i.e.*, 67 cm.

On the other hand, if a 1 : 1 ratio of calcium oxide to sulphur dioxide be assumed, no agreement whatever is obtained. If the results of Experiment 5 be used once more, the weights of calcium oxide and sulphur dioxide consumed would for a 1 to 1 ratio be 0.33 gm. and 0.38 gm., respectively. The resultant vapor pressure should be 404 cm., whereas that found was 427 cm., which on this basis would indicate that 23 cm. pressure was due to carbon dioxide. The carbon dioxide pressure at room temperature was found to be 45 cm., which at 130° C. would amount to 64 cm. The non-agreement is obvious. These preliminary experiments therefore tend to favor a relative consumption of calcium oxide to sulphur dioxide of 2 : 1 rather than 1 : 1.

It has been shown that carbon dioxide is produced during cooking, and a method has been described whereby carbon dioxide pressures can be determined. In the experiments performed, the volume of the vapor phase was known. Thus it was possible to calculate the weight of carbon dioxide formed during varying stages of the cook. No complete data are available for cooks of approximately four hours' duration, but Run 6 will serve to illustrate the possibilities inherent in this means of attack.

After a 13 hr. cook, the reaction cell in Experiment 6 was cooled down to room temperature, where the vapor pressure was determined before the cook was continued (6A, Table II). After a further 17 hr. cook, the cell was cooled to 25° C. and a vapor pressure determination made. A calculation has been made of the carbon dioxide produced per gram of dry wood. This was found to be 0.006 gm. after 13 hr., and 0.02 gm. after 30 hr.

It is of interest to determine whether the carbon dioxide was due to the decomposition of cellulose. In Experiment 3, pure cellulose was cooked in two steps. The first part of the cook lasted 10 hr. The reaction cell was then cooled to 25° C. and the vapor pressure determined. The cook was then continued at 130° C. for another five hours (3A, Table I). The first ten hours' cooking caused a pressure increase of 5 cm. in the system. This however was only 2 cm. above the calculated value. During the second step there was no pressure increase. This indicated that no carbon dioxide was produced. However, when wood was cooked under similar conditions, the pressure increase

due to carbon dioxide was found to be approximately 40 cm. This shows that carbon dioxide is a reaction product of the lignin or some constituent of wood other than cellulose.

It is possible to observe the color of the liquor during these experiments. At the end of the normal eight to nine hour cook, the liquor was still a clear straw yellow. However, after this period (beyond the maximum point on the curves), the liquor rapidly darkened. This indicated that a number of more or less complicated reactions involving polymerization were taking place. The change in the slope of the curves would indicate that these reactions consumed a large amount of sulphur dioxide. A study of Run 6 shows that after the pressure has continued to drop for several hours, it tends to remain constand for several hours, and then to rise. It has been shown above that the final increase in pressure is due to carbon dioxide formation. After the 30 hr. cook (Runs 6 and 6A) the contents of the reaction cell was black.

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